

*Stefan Fränze,
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Simone Wünschmann*

**Introduction to
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Stefan Fränze, Bernd Markert, and Simone Wünschmann

Introduction to Environmental Engineering



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Preface

To our students, teachers, readers and
whoever makes use of environmental technologies,

our textbook “Introduction to Environmental Engineering–Innovative Means to Clean and Protect the Environmental Compartments” is dedicated to an interdisciplinary approach toward the technical diagnosis, relief and avoidance of anthropogenic burdens on the environment by both inorganic and organic compounds as well as factors like waste heat, the diagnosis and so on being based on pieces of knowledge and methods from the natural sciences. This approach is going to be taught herein.

First of all, before even trying to remove or reduce environmental impacts by engineer’s means, there must be *environmental diagnostics* to estimate the kind, extent and reasons for the damage apparently done to the environment. This is achieved by appropriate measurement methods which often include, besides the chemical analysis of pollutants and interpretation of their possible ecological and health impacts, the development of novel methods in analytical chemistry and in effect research concerning eco- and human toxicology. This latter will give more information on the actual impacts of single substances on man and ecosystems.

Only thereafter should one switch to trying to design and implement measures in environmental reclamation (“*therapy*”) directly to relieve or reduce the environmental burdens or their very reasons by certain technical means or devices. During this, analytical chemistry must constantly survey the performance of these techniques.

A really big challenge—because it requires somewhat predicting the future—is *prophylactic* work against forthcoming environmental damage. Here, environmentally benign methods of production are chosen to anticipate and avoid actual environmental damages. For this aim, one must estimate the possible results and by-effects of different alternative or competing technologies to both the environment and to translate political ends—better sustainability, avoidance of public hazards, omitting some techniques or chemicals—into practical technical know-how and application in advance.

Obviously, some of these topics are quite complex to grasp. Hence we opt rather to “narrate” things, developments and options touching issues of *environmental*

diagnosis, therapy and prophylaxis in their respective historical context, to make you understand why people selected one technology (e.g., for vehicle propulsion) rather than another, thereby accepting environmental risks. Notwithstanding this, interested readers are fully supplied with definitions of terms and causes, formulas and tasks of comprehensive environmental technologies as they are in the third millennium so much shaped by information and communication technologies. But this is not a technocratic perspective: we also address ethical issues and juridical, political implications on national and global scales when musing what could be done to achieve a more sustainable, “greener,” yet responsible and libertarian way of life. Educating people with either facet of this issue (which we express; as a “dialogic education process” [DEP]) makes them familiar with the next chapter in this volume:

Starting with comparisons from general systems sciences as well as comparative planetology, features of the three environmental compartments atmosphere, water (distinguishing fresh-, sea- and groundwaters) and soil/sediment (regolith, respectively) are analyzed in terms of a chemical reactor concept (what happens, why, where?), pointing out chances and limitations put thereby on environmental sanitation. The specific chemical and biophysical properties of single environmental compartments thus logically define the levers to be used by innovative cleaning and protection methods devised and corroborated by engineering and natural sciences. Innovation criteria to be obeyed in this process include sustainability, compliance to existing and developing national and global legislation, and likewise cost-benefit calculations to come about with solutions which may later be accepted by societies as they are. But now for the more chemical part of the story: in order to understand what will or at least might happen, quite a number of basic chemical concepts must be discussed, including their messages for the Earth’s environment, such as redox potentials and their representation in Pourbaix diagrams, reaction kinetics (including Hammett and Taft equations) and the very concept of chemical equilibrium and dynamical (pseudo-)equilibrium. Early in this volume we learn about the *biological system of elements* which can provide tools for numerous unsolved problems in environmental engineering, besides understanding what happens in biology and bioinorganic chemistry.

The book is completed by case studies on process engineering dealing with certain environmental compartments, kinds of pollutants, which were admittedly selected partly due to the personal research foci of the authors:

Concerning the *atmosphere*, bioindication and biomonitoring are considered most innovative methods which will still gain importance in global-scale environmental surveillance. Of course, any discussion of problems now hitting the atmosphere as an environmental compartment would be far from complete if it neglects the issue of radiative forcing, global warming and in turn the possible methods to withhold the greenhouse gas CO₂ from the atmosphere during and after combustion processes.

A way of cleaning concerning all *soil*, aquatic sediments, air and water is phytoremediation, which received more scientific and technical attention during the past years, as did bioindication and biomonitoring. There are agents which can

secondarily mobilize toxic metals and other chemical species from the sediment owing to their own chemical properties, like complexation agents (ligands), among which the rather bioinert ethylene diamine tetraacetic acid and the chances to yet cleave it merit particular consideration.

Reactive barriers are a most promising method for cleaning ground-water bodies, hence their discussion in a separate case study. Another issue of growing importance and concern to freshwater supply and quality are residues of various pharmaceuticals. Both their environmental impact and the chances to remove them are discussed with the example of diclofenac (Voltaren™).

When (i) fossil fuels raise the problem of greenhouse gas emissions and (ii) nuclear energy poses accident hazards, in the afterwake of Chernobyl, Fukushima and less spectacular accidents, we become aware that an energy supply by other means becomes a key topic for our common future. *Renewable energies* like wind, water, solar energy and so on offer chances for increased use which are all technically feasible, affordable and sound in terms of natural sciences and engineering. To give an example, the Emsland region in northwest Germany, next to the North Sea and the Dutch border, and its features for renewable energies are discussed in one concluding case study.

This preface started with a request for global sustainability to be organized in a responsible way concerning environmental techniques and a “just” distribution of material goods and food among all mankind. While this just distribution and allocation by international trade will benefit from modern IT technologies, including the Internet, it also urges us to consider the human rights of all the others involved. Genuine citizens (citoyens) of the “global village” ought to represent mankind all the time in a manner of high responsibility, quality of behavior and statements and respect for global requirements. Theodor Heuss (1884–1963), first Federal President of the newly founded Federal Republic of Germany, maintained that “*quality means decency*”.

Dear readers, we are most aware of the large task we undertook by tackling the given topic of environmental engineering, even if it is just an introduction to this vast field. Possibly you are dissatisfied with the results somehow, be it for complexity of the issues, the way we choose to present them or for other reasons. In addition, there were some limitations given by the publishers concerning the size and presentation of this volume. Nevertheless we would like to emphasize that it was only due to the (almost) unlimited support given by Wiley/VCH and many internationally renowned colleagues—in both the practical and emotional sense of this term—over years that this book could be written in this form within a reasonable time. We would specifically mention Dr. Frank Weinreich and Mrs. Stefanie Volk, both with Wiley and Mrs. J. Klinkmann for the picture of the turtles. Many thanks to ALL who were and got involved in whatever way!

As we often address issues of scientific quality, we do sincerely hope to fulfill these standards ourselves, writing and illustrating our texts in a way to give best information to be grasped reasonably. The somewhat lengthy glossary and literature references contribute to this end and give hints for further reading. We would be grateful if reminded of both mistakes and didactic shortcomings possibly still

existing in this volume to overcome them in a next edition which hopefully will appear soon.

Thus, finally, we hope you enjoy reading this introductory textbook and get some information and the stimulus and encouragement for practically applying one or another of these possibilities we outline. We would be pleased to see this volume serve its (fairly ambitious) purpose in the study – and workplaces of some of you.

Zittau and Haren/Erika, Autumn 2011

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1

Definition, History, Discipline

1.1

Definition of Environmental Engineering

Environmental sciences strive to analyze and understand—by chemical and other methods—the influence of radiation (electromagnetic of various wavelengths, etc.), chemical compounds and yet other organisms on living matter and on those parts of Earth (crust, soil, upper lithosphere, hydrosphere, atmosphere) in which life occurs in an active form. In contrast, environmental engineering is meant to alter or exploit (environmental biotechnology, biological parts of sewage treatment system, etc.) these interactions to the benefit of humans and/or the environment. We shall see what this means. By biological activities, the above regions are profoundly changed; just consider chemical and climate effects of biogenic atmosphere components like O_2 , CH_4 , or the construction of vast coral reefs by organisms. *Environmental chemistry* deals with the “more chemical” features of this interaction and of processes which take part in the environment. It is the study of the sources, reactions, transport, effects and fates of chemical species in the air, soil and water environments, and the effect of human activity on these. *Environmental technology* is more the application of the environmental science and green chemistry to conserve the natural environment and resources, and to curb the negative impacts of human involvement. Sustainable development is the core of environmental technologies. This brings about the following definition of *environmental engineering*:

Environmental engineering is the technology concerned with the reduction of pollution, contamination and deterioration of the surroundings in which humans live, including environment and management of natural resources. This integrated management—beyond purification (waste or flue gas treatments)—includes reuse, recycling and recovery measures.

Accordingly, environmental engineering occurs at the interface of technical and environmental systems, and it requires a certain size of mass turnovers, even though the single devices may be fairly small if distributed among a multitude of individual pollution sources, like with catalytic exhaust gas converters.

Understanding chemical processes in the environment of course takes a sound knowledge of the array of compounds, ions and elements which are there, and of their distribution among the environmental compartments, which in turn controls

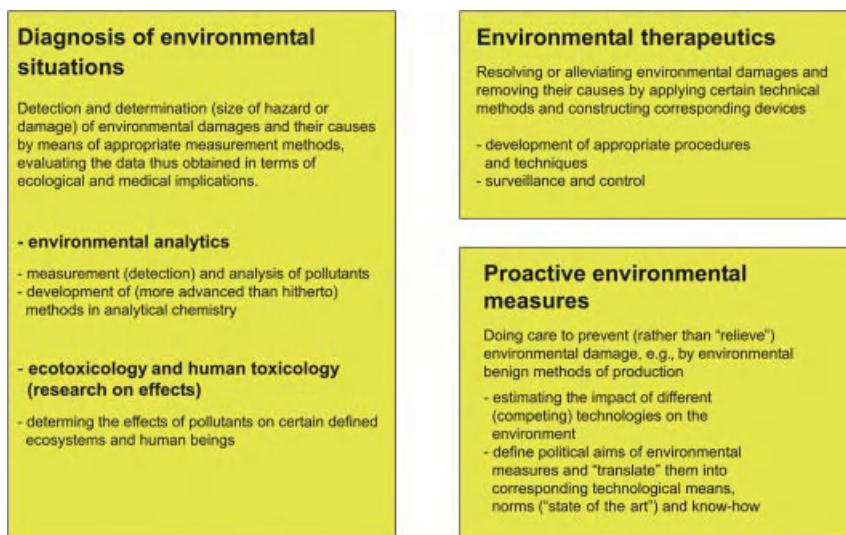


Figure 1.1 Diagnosis of environmental situations, environmental therapeutics and proactive environmental measures.

their exposure to secondary influences (e.g., UV irradiation, activation by chemisorption to, e.g., clay minerals). To obtain the corresponding information, lots of analytical data are required, that is, environmental analysis is warranted, while the secondary effects can only be described and evaluated concerning their implications for a realistic environmental setting by simulation experiments (Figure 1.1). Taken alone, it is rather pointless to determine the environmental half-life¹⁾ of some chemical species unless if one has sufficient additional information as to estimate whether some sink or source were apparently overlooked in modeling.

It is simple to demand more analytical data but, given the price of them, we are ever left with a pattern of sampling at rather distinct if not remote sites which must be linked by an extrapolation which fulfills the criteria of representative sampling. Expenditures for analytic data and therefore knowledge on environmental states being thus limited, we yet must go on to do "therapeutics", that is, the sanitation of obvious sources of pollution; and we must also abandon the use of substances which will cause hazards and damages only much later and at remote sites (global distillation causing PCB accumulation in the Arctic, ozone destruction, etc.). Hence proactive measures have to supplement cleaning up the more obvious mess. Surveillance and control—that is, analysis—are necessary in every stage of this development, to see whether the measures taken so far were successful.

1) The very term half-life includes the assumption that the decomposition processes are unimolecular, like photochemical decomposition via some

excited state or decomposition in adsorbed state or the cleaving agent is present in large excess (which holds for O₂ but not for any radical like OH, OCl, etc.).

Ecotoxicology thereby provides information which opens the view from mere chemical interactions and aspects of accumulation due to physicochemical properties to effects on single organisms and eventually to the effects these have for entire biocoenoses, causing members of one of many species to vanish, become less vital or conversely reproduce and spread by masses. The latter also can bring about chemical effects: the algae and cyanobacteria (phytoplankton) which form in response to eutrophication deliver *inter alia* chlorinated hydrocarbons which may attack ozone and certain poisons (red tides).

So let us now have a look at how we ran into the present situation and how far environmental engineering is a convincing response to demands produced by vast socioeconomic changes, some of which started more than 10000 years ago.

1.2

History and Development of Environmental Engineering

There is an extended prehistory of environmental engineering since people started reshaping their environs, which in turn required some measures to live so in an at least partially sustainable way.²⁾ The onset of agriculture in the Neolithic revolution enabled humans to gather in larger groups and to organize—now associated with agrarian areas—in correspondingly larger and less provisional settlements, distinguished by dwelling in stone houses now rather than mere wind-shelters (Koobi Fora), tents or cave entrances. The earliest of these which could be dubbed villages or even towns had a few hundred inhabitants each, like Lepenski Vir (Serbia, River Danube Iron Gate, site now inundated), Jericho (Palestinian Autonomous Territories), Çatal Hüyük (Turkey) or Poliochni (Lemnos Island, Greece; Tine and Traverso, 2001). Already then and there the increasing necessity to obtain wood, alter the landscape for agricultural purposes and later also to process ores caused damage to the local environment. In addition, people started to change their surroundings on some scale beyond felling trees, for example, when growing rice in man-made paddies—the earliest instance of “constructed wetlands” (given the first ones were located in the Lower Mekong area, beavers could not have given the idea for this innovation), with mining also dating back at least to the Mesolithic on various sites.

With larger extents of settlements and of corresponding production requirements, people had two choices:

- 1) Re-introducing migratory habits (slash and burn agriculture in a way replacing the former striding around with the game animals, on a somewhat longer timescale of relocation—a few years rather than months);
 - 2) More massively using and reshaping the local and regional environments (and to defend them, using the novel skills of metal technologies). These conflicts
- 2) Sustainable but not forever, yet lasting much beyond the present irreproducible resources, falling short of full replacement by regenerative matter and energy supplies.

are discussed, for example, in the Biblical stories from Genesis—Kain and Abel, and Abraham looking for a permanent place at which to live his personal culture and religion—and those conflicts which arose between Canaanites and semi-nomadic neighborhood tribes.

When they decided to do the latter, ecological problems associated with human activities were bound to aggravate even though the population used to increase but slowly then (in fact, the Neolithic revolution brought about a *decrease* in both average life expectancy and the chances of a child living to adulthood). In the other case nomads had to spread over vast territories, including use of force (the latest and most prominent example of a society of herdsman behaving like this being the medieval Mongolians under the Khans Cengis, Moengke and Ugedei, creating a huge yet ephemeral empire).

Either way, the environment received scars, and more than that (Thüry, 1995). Things got so bad that rulers were to set and enforce laws controlling the ways and sites of doing mining and ore processing, for example, while yet other innovations were to replace hitherto used “soft”, benign technologies of propulsion, travel and power supply (wind and water mills, animal muscle power, horse coaches, sailships, etc.) with more demanding—and polluting—ones like the steam engine and its derivatives. While “fuming” smokestacks were considered then—and often still even much after World War II—as an incarnation of progress and prosperity, people started to adopt the very technologies at hand for quite different purposes—and the same basic results of science—for improving the often dramatic, life-shortening state of environmental affairs, acknowledging there were no alternatives since now billions of humans (the first billion completed about 1830) were trying to make a living on this planet (Table 1.1).

International politics even today struggles with conflicts of distribution arising by this situation. Environmental technology—and environmental engineering as a operational branch feeding on it—thus became yet another facet of a “technology stalemate”, distinguished by the fact that about the same kinds of technologies were meant and employed to tackle the problems which hitherto contributed to creating them—except perhaps for electrical propulsion (which was not at all “green” then³⁾) and the use of chemical catalysts/filters for cleaning smoke gases and the like. Technology and environmental engineering thus kept a Janus face. In fact, neither a technology nor any kind of instrumental gear for (chemical) analysis was ever invented primarily for the purpose of improving the environment but taken from quite different ends and modified correspondingly, if at all: now soil cleaning is done using very much the same methods used in mining.

- 3) Consider the following facts: electrical energy storage—electricity taken from coal power plants rather than wind—took lots of highly toxic metals (Pb, Cd) then, if direct current was not even produced by releasing

toxic gases, like NO_x in the zinc/nitric acid/Pt battery, conversion efficiencies in motors were low (often, <10%), less than in mid-nineteenth century steam engines.

Table 1.1 A short description of the key cultural and socioeconomic changes, their environmental implications and the responses of rulers, society and scientists to tackle the problems.

Point of time/ period of culture	Event	Impact on environment	Remedy	Remarks
Mesolithic (≈25 000 years ago)	Extinction of big predators threatening and competing with stone-age hunters (cave and marsupial lion, giant monitor lizard <i>Megalania prisca</i>)	Trophic pyramid on solid land was essentially decapitated, changes in population structures aggravated by subsequent glaciation period		
Neolithic (≈10 000 years ago)	Revolution onset of agriculture, cattle- breeding, first larger permanent settlements, first production of synthetic structural materials (ceramics, metals/alloys of Pb, Cu, bronze)	Thorough change of land use, conflicts between hunter- gatherers and nomadic herdsmen here versus farmers there ^{a)}	Migration of tribes or other social units running into difficulties at stationary sites	
Ancient (3000–2000 years ago)	Large cities (Babylon, Rome, Alexandria), large-scale forest cutdowns, centralized infrastructures become labile in these large cities	Massive deforestation around large cities and all over the Mediterranean, peasant and native rebellions in Assur, Roman Empires		Consider (Hebraic) Bible, ancient eposes (Ilias, Edda) for recollections of the effects
Middle ages (5th–13th century)	Mass migration, opening new areas for agriculture, farming and cities by extensive deforestation, large-scale mining	Possibly climate change by deforestation	Ban of sulfide ore roasting in forests (14th century), official regulation of forest/wood use conflicts	
Industrialization (onset about 1730)	Invention of (direct- acting) steam engine, large-scale use of coal, extensive mining, development of large-scale chemistry and technology (factories replace small enterprises)	Greenhouse effect, decrease of rainwater pH, London-type smog, massive pollution of rivers by dumping chemical residues	Almost none, except for a reforestation program which essentially brought about monocultures of “cash crop” trees (spruce, beech, etc.), later definition of some protected areas; Yellowstone area as first National Park in the world	People thought about smoking stacks as a (the!) symbol of economical as well as social progress

(Continued)

Table 1.1 (Continued)

Point of time/ period of culture	Event	Impact on environment	Remedy	Remarks
Modern (since 20th century)	Megacities, chemical industry, N ₂ hydrogenation for fertilizers (Haber–Bosch process), problematic use of biocides, periodic oil spills, excessive whaling and fishery, individual traffic by cars and airplane use, production and discarding of “hard to biodegrade” polymers (“plastics”)	Eutrophication, partial destruction of marine trophic chains, effects of endocrinic agents in aquatic and land environments, air pollution, increase of greenhouse effect, damage to ozone layer by Cl photochemistry	Ban of certain compounds (CFCs, TBT cation, polyhalogenated aromatics, biphenyls), introduction of car exhaust gas cleaning devices, attempts to replace fossil hydrocarbons for solvent and traction uses with biogenic (“green”) substances	Attitudes changed once effects became both regionally intolerable and impossible to look the other way (about 1970 ^{b)})

- a) See the Bible (Genesis 1) for an archetypical description of this conflict which still has the potential for manslaughter and war even today (Cain vs Abel).
- b) In (Western) Germany and all of central Europe, the first time the old consensus was replaced with another vision (“Let us have blue skies over River Ruhr once again!”), a plea for different ways of essentially post-industrial, post-mining living in an old pit area, was put forward during the 1961 Bundestag election campaign of Willy Brandt (Social Democrats; election rally at Essen, 28th April 1961). The Greens appeared in the late 1970s.

Environmental sciences thus are secondary in their development, as also is evidenced by the times when concepts now considered to be key terms were introduced in to the literature:

Ecology	(Haeckel, 1866; Wallace, 1876; Junge, 1885)
Environment	(rather than “Außenwelt;” Uexküll, 1909)
Biogeochemistry	(Vernadsky, in the 1920s)
Ecosystems	(in the 1930s)
Geocology	(in English, rather “landscape ecology”, encompassing most sciences concerned with understanding and improving the environmental status; Troll about 1935)
Ecotoxicology	(Truhaut, 1969)

So it is a fairly recent approach, things becoming more disturbing when, for example, you compare the discussions about future ways of car propulsion (then, steam, or internal combustion engine or electric) in the first decade of the twentieth century to that of today—comparison often is really disgusting here! In many cases the actual impact of innovations in environmental engineering does depend less on what is technologically feasible at a given point of time—or at least appears to be so

disregarding limitations, for example, of catalyst resources⁴⁾—and more on political decisions. So the public recognition that there is some technology at hand to overcome a certain challenge or control a given pollutant—the key topic of applied environmental engineering—does not at all suffice. Rather, an environmental engineer has to consider aspects of political will and acceptance also: if nobody wants to have large-scale wind energy power plants or nuclear reactors “in his/her backyard” (or are afraid of the latter or of possible leaks in CO₂ deposition), it is outright futile to argue how much CO₂ emissions could be avoided or “passivated” by these technologies per MWyear (megawatts × years). Once people staunchly disagree on the very issue it becomes impossible to alter environmentally pertinent modes of behavior or supply strategies on relevant scales, at least not in democratic societies.

Environment contains hardly numerable different chemical species; in atmosphere alone some 70 compounds—excluding radicals and other short-lived intermediates—were detected and quantified so far. In the very moment analytical methods to determine parameters such as pH, redox potential and so on are used in the “open” environment, they will make their way into both methodology and thinking in environmental sciences. As a result, concepts from chemistry and (later on) cybernetics, systems sciences are going to be transferred into environmental sciences for some 170 years now at least, beginning with Liebig’s 1840 famous *Agrikulturchemie* (agricultural chemistry) and Schoenbein’s pioneering work on atmospheric chemistry, including discovery and atmospheric determination of the ambient oxidant ozone. Some observations, including detections of elements oxygen and nitrogen, and giving names to them according to their effects on (aerobic) organisms in pure state [for nitrogen, in German = *Stickstoff* (asphyxiating agent), in French = *azote* (not supporting life)] even date back much farther into the eighteenth century.

Examples of this conceptual “spillover” to the benefit of environment and its understanding include:

- Theory of chemical structures, implying/postulating that, most notably in isomeric compounds such as glycine and nitroethane or (Liebig’s classical) cyanate/fulminate couple, the unlike spatial arrangement of atoms and presence/absence of certain functional groups will bring about quite different physical and chemical properties (reactivity, toxicity, modes of decomposition) of otherwise identical chemical substances;
 - Ionic theory of electrolytic conductivity (most important for aquatic organisms which will often reproduce only within a given narrow range of conductivities);
- 4) For example, known and presumed platinum group metal (PGM) deposits would never suffice to endow all the cars presumably bought by Chinese or Indian citizens in the next 15 or 20 years to come with catalytic converters—let alone produce hydrocarbon- or alcohol-converting fuel cells for propelling most of them—and known amounts of lithium (Bolivia, Chile, Afghanistan, etc.) would also fall far short of electric car battery demands then. Accordingly both storage and conversion and exhaust gas purification techniques require much re-consideration for a large-scale application indeed (unlike with platinum group metals, Li extraction from seawater might prove feasible).

- Involvement of radical chains or ions in reaction mechanisms;
- Coordination chemistry (bioinorganic chemistry in life sciences as soon as essentiality of metal ions was linked to their forming catalytically active complexes inside proteins);
- Cybernetic systems analysis;
- Feedback patterns.

Actually, by proving there were no chemical elements whatsoever in living beings other than those already detected outside of them, biochemical and environmental analysis gave the final blow to vitalism, after Wöhler's demonstration that compounds like urea or oxalic acid could be prepared also by man rather than inside living creatures: biology, biochemistry, biophysics adhere to the same (and no additional⁵⁾) laws of nature as physics and non-biological chemistry do. Even after abandoning the vitalist assumption of particular rules life would follow, most (potential) environmental scientists still hesitated to transfer the rules and laws of physics and chemistry to systems shaped by biological activity mainly to a full scale. Much time after running the risk to be accused of adhering to either "materialistic" or "idealistic" prepositions (depending on which side of the former Iron Curtain you happened to grow up, live and work) came to an end, this reluctant attitude still poses obstacles to both understanding environmental processes and doing practical, efficient protection measures. In addition, education—starting at school at age six—suffers from people being reluctant (and often hostile) to link observations from different areas to each other, rather dealing with them as if they were completely isolated and independent of each other. For example, a class could have 45 min of chemistry, then 45 min of sports, music or some language, then yet another 45 min (topically unrelated again) of biology and so on. Thus young people are (often permanently) misshaped in their thinking and corresponding attitudes.

In a similar way, each model designed to describe some complicated system—be it an environmental compartment such as air, a biocenosis, an ecosystem or "just" a single organism—both stresses and neglects certain (mostly many) aspects of it. Both mere description and operational approaches, say, environmental biochemistry and environmental engineering, suffer from this likewise, the latter often even more strongly. Consider an example from medicine to understand this: there is a case of massive cardiac arrhythmia, possibly threatening the patient's life and anyway causing deep sorrows to him/her, going to be tackled by specialists from different areas of medicine. Psychologists will try to "understand" which circumstances caused the condition now manifest as physical illness while a cardiologist might try to fix the problem in and by treating the muscle itself, the former possibly suggesting family therapy while the latter might implant a cardiac

5) In fact, Fränzle (2010) undertook to analyze biochemistry, biocatalysis and reproduction along very basic physicochemical rules concerning structural complexity and

chemical feedback, unveiling some principal limiting conditions for life—on whatever chemical basis—to operate and on the establishment of essentiality.

pacemaker. Likewise an environmental chemist is going to address, correct and fix other features of some impaired environmental system than people stressing aims of “landscape quality” – with the latter working in a manner quite as “scientific” also! Returning to the former example, neuromyology and psychosomatics deal with different scales of embedding phenomena (the entire body or even the social surroundings vs the sinus node of the heart), quite like in the latter (from molecules to landscape dimensions).

Either approach is fully justified and also important: providing electrical stimuli may be pivotal to keep the patient alive even if the infection disease or personal conflict underlying the heart problem were neither diagnosed nor resolved so far. Quite similarly it is impossible to meet ambitious ends concerning landscape quality as long as the corresponding parts of the environment are subject to massive chemical burdens. Rather than considering one approach “better” or “worse”, we should acknowledge there are different – if not complementary – options which draw upon various different ways to analyze a given environmental problem.

Thus, one can actually take notions of esthetical and sensorial perturbations as warning signals, prompting us to tackle a poor situation [vegetation which succumbs to pollution across vast areas is considered “ugly”, as are mass spreadings of a few pollution-resistant species (nettle, algal or cyanobacterial blooms), while polluted air and water reduce both physical and psychical well-being of people exposed]. Luckily, man is not a particular sensitive bioindicator; however, detrimental effects of pollutants toward vegetation were noticed early, correctly linking these to human activities, especially mining. For examples from old history, consider remarks on damage to forestry and lichens in mining areas.

Pliny the Elder already noticed that mining of certain ores released gases which damage vegetation, the production of such gases being related to the presence of sulfur (and its oxidation as we now know). The active plant poison mainly is SO_2 , possibly with admixtures and co-effects due to carbonyl sulfide (COS). The above observations prompted rulers (kings, dukes, bishops) in possession of large forest areas already in the Middle Ages to outlaw mining and ore processing inside either forests or human settlements. In addition, lichens were noticed becoming rarer and eventually vanishing in industrialized, heavily populated regions such as London during the nineteenth century (i.e., subsequent to the industrial revolution and thus vastly increased coal combustion rates). This once again was interpreted (correctly) to inform of increasing air pollution. From there, the topic soon made its way into popular literature, consider the numerous allusions to London “fog” (rather being smog in a very pronounced form) and its role in the plot of A.C. Doyle’s criminal novels of Sherlock Holmes⁶⁾ and his detective work.

As for environmental chemistry between about 1850 and 1940, some men should be mentioned who drove their brilliant and fundamental works on organic and physical chemistry, spectroscopy (IR, etc.), reaction kinetics and geochemistry

6) Most likely, a friend of Doyle’s who was one of the pioneers of both forensic and environmental analysis, J. Norman Collie (1859–1942), and who additionally claimed

to have discovered noble gas neon before Ramsay did, was the historic figure after whom Holmes was depicted (Emsley, 2001).

even further to investigate environmental implications of their discoveries, namely Christian S. Schoenbein, Svante Arrhenius (1903 Nobel laureate in chemistry), Volodymyr Vernadsky, Sidney Chapman and the Odum brothers. (This is not to suggest that women did no eminent work in the development of environmental chemistry and engineering, respectively, but apparently it is fair to state that it was less obvious in terms of some “inter-sex competition” than in, say, mathematics or radiochemistry/nuclear chemistry.)

C.S. *Schoenbein*, the father of atmospheric chemistry, also coined the term “geochemistry” (Kabata-Pendias, 2001). In 1840, he first produced and discovered ozone (O_3), later (1858) detecting it in tropospheric air also by iodide oxidation during balloon ascents, then finding yet other photooxidants such as hydrogen peroxide in rainwater. As for environmental engineering, it should be noted that he, at the same time (1839) but completely independently from Grove, developed the first *fuel cells*⁷⁾ using H_2 (Pehnt, 2002), while in applied organic chemistry he became famous as the inventor of “nitrocellulose” (rather, cellulose nitrate polyester) explosive.



Christian Schönbein (1799–1868)

- 7) From the viewpoint of environmental engineering, and given the almost practical state of affairs reached in the late 1830s concerning electropulsion of both cars and little ships, it is outright tragical that the first successes by Schoenbein and Grove using dihydrogen were not taken further to achieve ethanol electroprocessing by Pt mediator electrodes; instead it was tried (in vain) to achieve fuel cell electrocombustion of coal (which succeeded just a few years ago) from then on much into the twentieth

century. Such activated Pt surfaces, used by both Grove and Schoenbein, also were already then state of the art, for example, in zinc/nitric acid piles providing kilowatt power outputs. This would straightforwardly have provided efficient fuel cells operating on liquid biogenic fuels, rather than very heavy Pb accumulators or primary elements. But for this misdecision, fuel cell/electromotor propulsion systems would have successfully competed against the steam engine in propulsion very soon afterwards.

Being among the pioneers of IR spectroscopy, and following earlier suggestions by Tyndall (1872) concerning atmospheric and climate drawbacks of IR absorption by increasing CO₂ in the air, Svante Arrhenius pursued the question of climate effects of this CO₂ enrichment from 1896 onwards before quite unrelated work—advancing the ion theory of salts and its drawbacks for producing electrically conductive solutions and melts—won him a Nobel in 1903. Arrhenius's and Högbom's 1896 work on the greenhouse effect (Arrhenius, 1896) included all estimates of its anthropogenic share ("radiative forcing") from IR spectroscopy, expected extent of global warming and speculated about counter-acting climate secondary effects, such as changes of rainfall. Considerable public interest was arised by their corresponding demand to limit the burn rates of coal which had already by then caused massive environmental problems by SO₂ releases. In addition Arrhenius dealt with biochemical problems such as modes/mechanisms of toxin–antidote interactions or the chemistry of digestion. His formula to calculate activation energies yielded deepened insight into reaction mechanisms and to activation of chemical reactions.



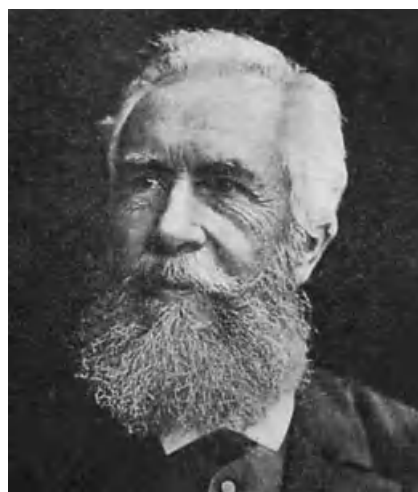
Svante A. Arrhenius (1859–1927)

The ecological paradigm, although explicitly based on considerations of matter and energy fluxes and balances, which was brought into biology by Junge and Haeckel about 1870, strangely was treated for quite a while as if entirely unrelated to chemistry. Junge (1885) discussed a community of organisms in its interactions considering a pond (*Der Dorfteich als Lebensgemeinschaft*—"a village pond seen as a community of living beings"). Haeckel defined ecology to describe or be *gesamte Wissenschaft von den Beziehungen des Organismus zur umgebenden Außenwelt*—"the holistic science covering the organism–outer world relations" [the term

environment (*Umwelt*) as opposed to outer world/surroundings (*Außenwelt*) was coined only much later, in 1909]. This way to cover and analyze outer relationships of an organism necessarily includes metabolic exchange due to breathing and feeding. This strongly suggests now to focus on exchanges of oxygen and CO_2 among fishes and water plants as a chemical process crucial for this biocenosis but the pioneers did not, then, possibly feeling the difficulties they would run into (without isotopic markers or the like at hand). Rather soon after Liebig had paved the way for this kind of reasoning by investigating the chemical processes in soil and in the soil–plant system, providing useful insight for agriculture, some chemical formulation of the ecological paradigm might be thought the more straightforward as aquatic chemistry was rather advanced already then. Accordingly one might anticipate chemical ways of thinking soon to be introduced into the emerging science of ecology, like they did in physiology, but this did not happen until some 40 years later when Alfred Lotka and Vito Volterra did use chemical models (borrowed from radical chain chemistry) to model population dynamics of two species coupled by predator–prey relationships. Soon after, beginning in 1916, Volodymyr (the original Ukrainian name, usually transliterated–Russian–as “Vladimir”) Ivanovich Vernadsky started integrating the views of biochemistry, metabolism and geochemical cycles on Earth which is influenced by biological activity, creating yet other feedback loops. Such feedback systems are capable of unprecedented dynamics, including oscillations⁸⁾ as Lotka pointed out, creating a



Friedrich Junge
(1832–1905)



Ernst H. Haeckel
(1834–1919)

8) Among chemical oscillators, however, it turned out to be very difficult to produce any which works along Lotka's rather simple feedback structure.



Alfred Lotka
(1880–1949)



Vito Volterra
(1860–1940)

new paradigm again, that of feedback control and cybernetics, augmented by the onset of electronics, both theoretical and technical (Turing, Wiener, Forrester) which in turn provided the means to analyze such systems efficiently (Forrester modeling, which soon made its way into ecology also), with the key parts of computers being prone to feedback control and amplification themselves (triode, transistor).

By using this feedback reasoning on the integration of metabolism into geochemistry, V.I. Vernadsky became the founder of *biogeochemistry* (this term being his, also), producing fundamental work on the involvement of living beings into Earthly matter cycles together with his school [now the Vernadsky Institute of Russian (formerly Soviet⁹⁾) Academy of Sciences]. Vernadsky's point of view was never restricted to single ecosystems but he covered the entire Earth from the very beginning, for example, postulating that biological evolution was (also) about introducing all the accessible atoms into biochemistry. He went so far as to consider the metasystem consisting of living matter and its environment as alive by itself. His focus on concentration of elements by metabolism of whatever organisms is essential to ideas and approaches like bioremediation, biomining and biological waste treatment now. His “basic biogeochemical rules” (he even called them . . . laws; Levit, 2001) refer to the fact that living beings, by reproducing and spreading, continue to absorb resources from all three environmental

9) By the way, Vernadsky also was (in 1918) the founder of the *Ukrainian Academy of Sciences*; and it is not quite clear why he eventually returned to Stalinist USSR in late

1927 after doing research and teaching in the West for about five years, including Berlin, Paris and the United States of America.

compartments to an increasing extent, partly binding them for about a lifetime, partly passing them through rapidly. The amounts of elements involved in such biogeochemical cycles used to be much larger than turnover by mining or similar anthropogenic activities until recently. It must be noted, however, that even now only a few elements in the biosphere are retained by living beings to a share of 10% or more (essential elements P, Zn, Cu; and highly toxic trace metal Be) while the biosphere represents some 1–2% of C, Fe, Mn available across the biosphere only and much less of crucial elements such as N, S or Mg.

A seminal work, never to be reproduced for any other larger part of Earth's solid surfaces, by Vernadsky and his co-workers/successors is his "Atlas of biogeochemical provinces of USSR", begun in 1943 and completed by Vinogradov. It covers that huge area of some 15% of Earth's solid surface completely and often highly resolved, except for Tajikistan and the Arctic coasts. Therein, "deviations" of levels of certain elements are linked by epidemiology to diseases of man and animals, and to the abundances of plant and animal species, some of them known to accumulate or at least tolerate substantial concentrations of these elements. This provides information pertinent to both health protection, toxicology and ecology. Using the remarkably high spatial resolution, for example, in the Caucasus areas allowed a definition of the needs and strategies for the remediation of polluted soils, ground and surface waters. Biogeochemical provinces as such may also be distinguished by and named after essential elements like manganese or zinc.



Vladimir Ivanowitsch Vernadsky (1863–1945)

Sydney *Chapman* originally was a mathematician but became intrigued with physics and chemistry of the upper atmosphere, likewise with influences onto Earth's magnetic field due to terrestrial and extraterrestrial events. He created the first (in 1930) model of photochemical dynamics of the ozone layer, which considered the oxygen species O, O₂, O₃, including excited states and hitting partners only. This part of the ozone formation/destruction cycle is still called Chapman chemistry in his honor, all the more recent additions of contributions of hydrogen-, nitrogen-, halogen and other compounds to these processes being just modifications and refinements of this classical model, which itself draw upon Bodenstein's theory of radical chain reactions. Rowland and Molina, primarily trying to understand the chemistry of O and Cl compounds in the stratosphere of Venus (Rowland and Molina, 1974), pointed out the possibly devastating effects of increased organochlorine (CHC, FCHC) and HCl inputs into the stratosphere of Earth and local photochemistry on the ozone layer soon after Chapman's death (in 1974), which earned them the 1995 Nobel for chemistry together with Paul Crutzen.



Sydney Chapman (1888–1970)

It is a classical way of thinking in atmospheric chemistry to consider Earth's atmosphere as a photochemical reactor (see Section 2.2.1), with the troposphere being essentially sealed to the top by the tropopause, to the bottom by the surface of the Earth. Thus, it is closed for rather fast processes like a closed chemical reactor; it takes several months for cross-equator mixing of some compounds specifically introduced on one or the other hemisphere (e.g., the lifetime of CO) whereas fully homogeneous distribution will not be attended unless the compound "survives" at least some five years in the troposphere (e.g., with CH₄, CH₃-CCl₃). Vertical mixing beyond the tropopause into the stratosphere takes even longer although the uneven levels of tropopause (some 8–9 km in Arctic and

Antarctic regions, up to 17 km close to the equator) allow for some “leakage” both of O₃ downward into the upper troposphere (where it is going to cause some problems in using compressed local air inside airplane fuselages and cabins) and vice versa of other compounds into the bottom layers of the stratosphere. Only such organics which are desactivated toward attack by OH radicals or photochemical¹⁰⁾ effects with respect to CH₄ with its five-year lifetime (Atreya, Mahaffy, and Wong, 2007) by corresponding electrophilic substituents (F, CHal₃, CN, NO₂, etc.), that is, FCHC, acetonitrile or nitrocompounds will make their way into the stratosphere from below,¹¹⁾ thereby escaping destruction over decades.

The Chapman chemistry now deals with radical chain processes, as outlined by Bodenstein and Lind (Bodenstein and Lind, 1906; cf. Laidler, 1970), and by this origin puts some emphasis—beyond Chapman’s simple model—on H abstraction and O transfer reactions of halogen compounds. This was first transferred to modeling the atmosphere by Chapman, at about the same time one could start to compare among atmospheres (and their possibly underlying chemistries and photochemistries) owing to the pioneering works on spectroscopy—and thus chemical composition—of planetary (Venus, Mars through Neptune) and satellite (Titan) atmospheres by Wildt (e.g., Wildt, 1932) and Kuiper (Kuiper, 1944). The simplified approach, just considering homogeneous gas-phase chemistry, omitted effects of aerosols, with heterogeneous catalytic chemistry then amply used in technical chemistry but very poorly understood. Accordingly possible effects of aerosols, from catalyzing recombination over interfering with acidic gas phase species [e.g., CaCO₃- or silicate-based particles (Wayne, 1991a), the latter silicates reacting also with hydrogen fluoride (HF)] up to photoelectrochemistry (injection of OH radicals, cleavage of organics by Ti and Fe oxides) were disregarded then, as were the contributions of ion–molecule reactions. For the latter, suggestions to consider

- 10) In the troposphere, admitting UV radiation only beyond (above) some 295 nm wavelength, there will be no photodissociation of either C-F ($\lambda \leq 190$ nm), C-CN- ($\lambda \leq 195$ nm), C-Cl- ($\lambda \leq 230$ nm), C-COOH- ($\lambda \leq 240$ nm, e.g., acetic acid) or C-Br- ($\lambda \leq 280$ nm) bonds; the situation is different with iodo- and to some extent nitrohydrocarbons, ketones and lower aldehydes which readily produce alkyl radicals, H and I atoms, respectively, besides other products like CO, NO₂.
- 11) In the upper stratosphere and mesosphere, there are admixtures of all CH₄, HCN, CH₃CN, HCHO besides water and H₂O₂ and various protonated (Kopp, 1990), acid-solvated and hydrated derivatives thereof, which likely do not come from the surface but are introduced by partial pyrolysis of (carbonaceous) micrometeorites up there. While this apparently is a natural phenomenon,

sometimes enhanced by “near misses” of large meteors/tiny asteroids like the 1965 Grand Teton Mountains (Wyoming) event, noctilucent clouds which are located at some 82 km above ground (i.e., at the level where both unmixing of lighter gases H₂, He, Ne and O atoms from heavier and more familiar N₂, O₂ starts and the local ion concentration begins to increase) were not observed until much after begin of industrial revolution, not even temporally linked to large volcano eruptions.

Accordingly, noctilucent clouds must be considered to give a hint at least that atmospheric pollution did propagate into the upper stratosphere already during the nineteenth century, especially increasing its content of water vapor with correspondingly increased photoproduction of H atoms and OH radicals, contributing to attack on ozone, as does warming of the stratospheric regions.

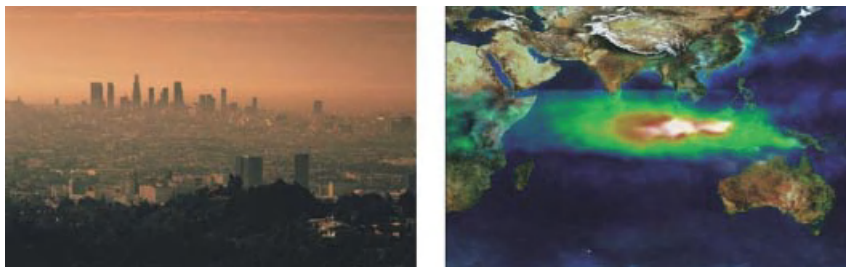


Figure 1.2 Discoloration and increased turbidity of atmosphere due to combustion taking place nearby. Left: Smog in Los Angeles due to car traffic mainly. Right: Slash

and burn agriculture in Indonesia (Borneo) getting out of control, in 1999. Colors encode different levels of smog pollution. Photos: Environmental Protection Agency, July 1999.

them were introduced by cosmochemistry in the early 1970s (about the time of Rowland and Molinas' seminal paper, in 1974), like for the theory of smog formation, concerning both Los Angeles smog (Figure 1.2, left part) produced by photooxidants¹²⁾ including their secondary chemical interactions and London smog, distinguished by formation of polymeric, mainly organic substances (PAHs, soot), likewise. Both technical combustion processes and natural ones, for example, forest wildfires, cause aerosol and smog formation (Figure 1.2, right part).

Generally speaking, feedback analyzes provide quite another concept of causal relations than the classical linear "A causes B, then happens C due to B" and so on since feedback allows for some kind of regulation of the state of a system, permitting compensation for external perturbations or otherwise responding to them (excitability). The branch of science which analyzes structures and feedback pattern/effects in feedback causal system (containing causal loops) is called cybernetics. As a paradigmatic concept, cybernetics arised only about 1950, even though technical devices which involve feedback regulation were invented as early as Greek ancient times, for example, to control water levels (the water closet flush preserves this construction up to today). Later, during the development of power-producing machines, similar devices were introduced by Watt (in 1766) for stabilizing the work rates of such steam engines: a rotating device controls steam inlet rates by shifting a valve position according to centrifugal forces, keeping running speed and power release of a direct-acting (i.e., non-atmospheric) Wattian steam engine constant unless the operator changes the parameters.

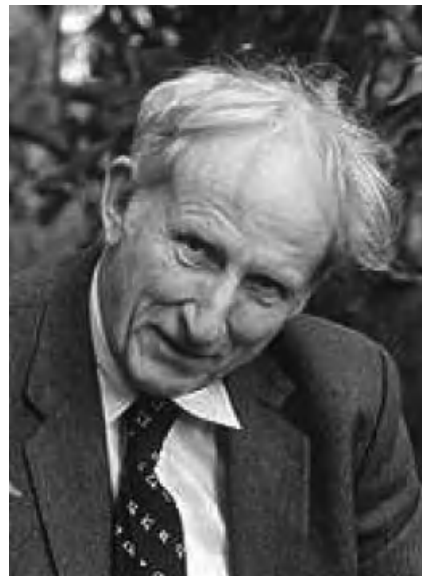
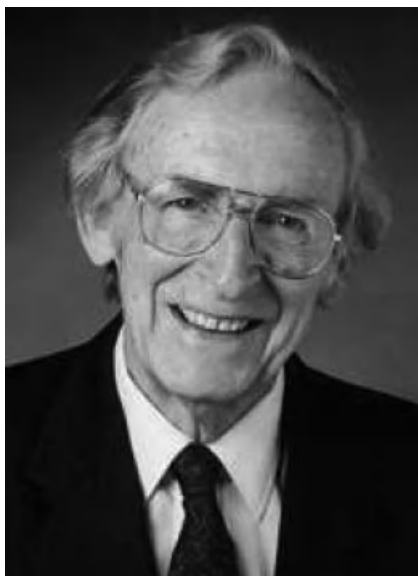
Though the idea of feedback is essential to the entire concept of ecology in biosciences, transport of matter through an ecosystem was considered otherwise, that is, to be mainly linear, for example, speaking of trophic chains rather than trophic nets for long although there is considerable feedback by fungi and bacteria,

12) Note that not all "photooxidants" behave as oxidizing compounds after their formations: while this does apply, for example, to ozone, peroxides like H_2O_2 , or NO_2 , condensates thereof like peroxyacetyl

nitrate, or nitroaromatics present in rainwater, there are other photochemical products, including formic acid $HCOOH$ and aldehydes $RCHO$, which are reductants, rather.

for example. Cybernetic approaches were only later (during the 1960s) introduced into biology, prominently by the Odum brothers.

The principal contribution by the Odum brothers, *Eugene P. Odum*, and *Howard T. Odum*, was to transfer the concepts of energy and matter flow and the ways in which it is controlled in technology including electronics to ecology. H.T. Odum, for example, started his work on what was to become systems ecology with quite classical treatises on an element cycle, namely that of strontium (Odum, 1957), and what it was to tell about larger-scale biogeochemical processes and interactions. Similarly he proceeded to use that horrific extent of radioactive pollution at the United States Eniwetok nuclear test site, with the radionuclides [e.g., ^{90}Sr , ^{65}Zn , rare earth elements (REEs), Pu] also present in the organisms living (or rather surviving) there, for analyzing matter flows in corals and others (Young, 2005). Moreover, they were among the first to use and then popularize the term “ecosystem”,¹³⁾ H.T. Odum additionally introducing the term and concept of ecological engineering (somewhat different from the title of this volume). The enrichment of an element in some volume of matter (be it an organism or something else) being controlled by thermodynamics [a partition coefficient between two phases (one or either of which may be biomass; Fränzle, 2010) is a matter of free-energy differences and thus chemical thermodynamics, solvation or speciation energies] directly led to the notion that energy flows and general thermodynamics were also to shape ecosystems. Their particular emphasis was with the interactions and relations among ecosystems.



Eugene and Howard Odum (1913–2002, 1924–2002)

- 13) The case whether an ecosystem does actually “exist out there”, rather than be a set of interrelated elements singled out for interpretation purposes by man (scientist) only, may remain open here. It was addressed only much later.

Energy flow in ecosystems and individual organisms and the way it shapes them and their “strategies” is a key concept here, postulating living beings to be optimized in terms of maximum power output rather than utmost efficiency of power generation. Energy and matter storage are accomplished by organisms to survive periods of intermittent energy supply, such as interruption of photosynthesis during night. Analogs from electrical circuit theory, for example, Kirchhoff’s theorem, and from open-system thermodynamics were taken—in a way which remains somewhat controversial—to corroborate the results of the first full-scale measurements of matter and energy flows done by them also (“Silver Spring Study” in Florida, 1972), leading them to postulate additional laws of thermodynamics for purposes of simulating and understanding ecosystems. Thus they made the basis for quantitative understanding of ecosystems operation, including thermodynamic fundamentals governing chemical and photochemical energy conversion, within and beyond the realm of biochemistry.

The shape of the models was suggested by the analogy with electrical circuits, accordingly ecosystems were treated as if containing elements like diodes, switches and energy supplies also.

Now let us turn from discussing individual people to looking into some organizations.

NASA, the National Aeronautics and Space Administration of the United States of America, founded in 1958, in response to the Soviets having launched the first artificial satellites of the Earth before the Americans managed to do so, ever was both a political and a scientific organization (Zimmer, 1996). Anyway, many features now commonplace in their everyday implications for remote sensing as well as communication were introduced by NASA and military satellite applications in the 1960s in the United States, with comparative planetology, enabled by Earth-based astronomy, NASA and Roskosmos alike (Chertok, 2002), providing lots of additional information on both the state of the environment and perspectives to modify and improve it. Polytetrafluoroethylene (PTFE) coatings of frying pans were not due to space research, as common wisdom has it, having been available since the late 1930s, but:

- satellite-based weather forecast, other applications of remote sensing,
- photovoltaics,
- compact high-power fuel cells and
- autonomously operating research vehicles, also of much use in both ocean research and control of highly dangerous man-made environments such as the interior of nuclear powerplants

are indeed due to space research to quite an extent. Thus, though shaped by both instruments (large long-range rockets had been originally constructed for deterrence by nuclear warheads they also could carry) and propaganda purposes of cold war (the race to bring a human to the moon first hardly was motivated by any scientific interest in lunar research, and it produced huge devices no longer of any military “dual use”), NASA and its Soviet counterpart did—and still do, now

augmented by cooperation and others (Europe, China, India, Japan) being also involved—a brilliant though most expensive job in both research pertinent to environmental engineering and in making people aware of the hazards our planet is exposed to by man—and what needs to be done in a hurry; that small blue ball apparently soaring over the lifeless, barren surface of Moon.

Irreversibly changed people's notion of themselves and their surroundings, as later did satellite-derived pictures of, for example, atmospheric (NO_2 maps) or ocean pollution.

1.3

From Environmental Chemistry and Technology to Environmental Engineering: Understanding and Diversifying Anthropogenic Environmental Influences

As outlined before, environmental chemistry deals with understanding chemical processes in the environment while environmental engineering is about tackling present problems in more general ways, also more general concerning the applied methods. Given the extreme but rather frequent case that “pollutants” emitted by nature and man (anthropogenic) are identical, say the parallel emission of solvents chloroform (Gribble, 2005), acetonitrile produced by marine algae and by forest fires, respectively, or that of acid precursors SO_2 and HCl by volcanoes, the “acceptable burden” of environment is just beyond human decision. For example, CO is subject to the same chemical (cleavage by OH radical), photochemical (addition of excited ^3CO to C–H- and O–H bonds) and biochemical processes (oxidation by CO dehydrogenase) whether it originated from volcanoes, engines, coal pits (desorption) or incomplete combustion. Fortunately, while any remediation beyond just saying what happens to CO molecules in the tropos-¹⁴⁾ and biosphere requires knowing where and how much is emitted—and then changing these processes or do end of pipe remediation if feasible, the sources are irrelevant for end of pipe strategies if not directly fitted to the device which emits CO.

This superposition of “natural” and anthropogenic burdens to environment requires to *minimize* inputs as we cannot control the extent of algal growth (except via reducing eutrophication of shallow sea areas) or even that of volcano eruptions. Understanding in environmental chemistry then is understanding the fate of some compound regardless of its origins, concerning all processes, reaction patterns, mechanisms and eventually sinks (and their respective capacities) while remediation obviously must be focused to large-scale or/and high-concentration emission sites and sources. Remediation strategies have to consider specific properties of pollutant sources, like the processes which give rise to some unwanted compound there.

By definition sources release some material, making any structures which act as sources open systems. Technical systems are open ones, too, exchanging both

14) The tropospheric lifetime of CO is about half a year so it will not propagate upward into the stratosphere.

matter and energy with their environments much like living beings do but often at much higher spatiotemporal rates, mainly because temperatures can be attained and used for fulfilling the corresponding task which are beyond biological acceptability. This is why, say, a 100 kW car engine is much smaller (by almost two orders of magnitude) than a whale whose muscles deliver comparable power—and thus similar amounts of CO₂. When, which often happens, other materials are used in technical devices than in biology, materials which are beyond biochemical synthetic capabilities, for example, metals, their production and eventual disposal must be included in any cradle to grave consideration. Then arguments reach far beyond thinking about energy efficiency. In addition, there are less criteria for a technical system not prone to withstand evolution:¹⁵⁾ if plant leaves would not gather much more organic carbon by CO₂ reduction than is required to make them, plants would simply not exist while the total (lifetime) electric energy delivered by photovoltaic cells being in excess of that required to produce high-grade elemental silicon or Si hydrides,¹⁶⁾ gallium chloride or trimethylgallium and AsH₃, SbH₃, respectively, had just to be demonstrated secondarily.

Anyway, an open system is distinguished by exchange with the environment, which has thermodynamic drawbacks (certain equilibrium assumptions do no longer apply) and other consequences:

- energy (often, electric currents such as in electrochemistry) and raw goods or energy carriers/reductants or oxidants¹⁷⁾ must be admitted in a controlled fashion, while waste heat and
- matter products as well as waste products (gases, condensed wastes, ashes, by-products like slag in ore-processing) have to be (steadily) removed from the system or device.

Accordingly, typical devices of environmental engineering are open systems, too. Moreover, they are—at least for end of pipe remediation systems—attached to yet other flowthrough, that is, open systems, for the best purpose of cleaning their

15) Except for effects of market competition, of course.

16) The familiar blue, perceptibly polycrystalline “silicon” solar cells are not made of elemental silicon altogether but rather from hydrogen-containing polysilicon hydrides of approximate composition SiH_{0.15}, prepared by controlled pyrolysis and simultaneous dotation of lower silanes such as Si₂H₆, Si₃H₈ (pyrophoric compounds, by the way) which in turn are made using SiO₂ and elemental aluminium, sodium hydride, H₂ (Riedel, 2004) according to $3 \text{ SiO}_2 + 4 \text{ Al} + 4 \text{ H}_2 \rightarrow \text{Si}_3\text{H}_8 + 2 \text{ Al}_2\text{O}_3$ (simplified) in a LiCl/NaCl/NaH melt, demanding the energy to produce the above reactive elements (e.g., for Al, >20 kWh/kg).

Two common examples: (i) hard coke is used in iron high kilns as a reductant providing the reaction energy to maintain the heat of the system by chemical heating (some 1600 °C, beyond iron melting point, and be it by admission of some air, causing direct C combustion), while (ii) chlorine in organochlorine chemistry acts as both oxidant and reactant by being added in chlorinations of organics like C₂H₄, benzene or CS₂ (even if methods and/or products are outdated now). Here, while elemental C can be obtained from nature (hard coal) with minor modifications, lots of electrical energy is required to obtain elemental Cl₂ from alkali halide brines at all, linking the eventual oxidant/reactant function to prior input of electrical energy.

outputs. In the practical case that an internal combustion engine or fossil fuel powerplant employ air rather than neat oxygen for oxidation of the respective fuels, the combustion chambers will also ingest (very considerable amounts of) N_2 along with O_2 ; in addition some of the fuels (lignite, gasoline) also contain organonitrogen compounds. Combustion (air oxidation) of the latter will afford NO, as will another process: at sufficiently high temperatures (in excess of some 1300°C) N_2 gets thermally excited into a higher electronic state (loosely, N_2^*) which then either emits ultraviolet radiation ($\lambda = 337\text{ nm}$) or reacts with a variety of chemical species which are present in a combustion chamber, including O_2 ($\rightarrow$ NO), CH_4 ($\rightarrow$ HCN) and so on.¹⁸⁾

Release of NO is obviously due to internal combustion engines being open systems (equilibrium concentrations of NO being extremely low, and what is produced in the heat is “frozen out” by release from the chamber, in case of two- or four-stroke combustion engines this freezing is enhanced by (almost) adiabatic expansion of the gases above the piston, producing cooling rates $\gg 10^5\text{ K/s}$). Nitrogen is put into the motor in various chemical forms, parts of it to be released as NO_x . In hard-coal powerplants, both contributions from oxidative and thermal NO are comparable in size. Of course, the same consideration holds for all other chemical elements present in either fuel or air provided they are chemically reactive at all (e.g., release of HCl, etc. from salt coals).

If open systems (technically speaking, reaction–diffusion systems) are connected to each other, non-linear behavior may result even if there is no “real” feedback of the second system into the first. The prime consequences are:

- 1) Such throughflow systems never attend “genuine” chemical equilibrium, since chemical equilibrium is (can be) defined for closed systems only. Therefore not only products of doubtful thermodynamic stability are produced during, for example, technical (engine) combustion, adding to the list of potential pollutants afforded there, but in addition one must make sure that (once-again, throughflow, hence open-system) chemical or physical (relying, e.g., on adsorption) transformations meant to remove these pollutants will operate fast enough, that is, while the reaction mixture is still within the device.
- 2) Patterns of uneven reactant concentrations may form, rendering the performance of (too) small heterogeneous catalyst devices essentially unpredictable or prone to temporal oscillations of concentrations of formed intermediates.¹⁹⁾

18) HCN fortunately undergoes further combustion to yield additional NO, while higher hydrocarbons $\rightarrow$ nitriles. Thus nitrogen oxides, NO_2 being produced by NO contacted with (external, cold) air, are formed by both direct oxidation of N-organics (“oxidative NO”, plus those formed involving N_2^*) and thermally induced reaction (“thermal NO”) between the elements nitrogen and oxygen (note that for ground states, equilibrium lies far

to the left, which would cause the highly endothermic NO molecules to decompose almost completely into N_2+O_2 if it were not for this reaction being spin-forbidden).

19) By Onsager’s theorem, oscillations around chemical equilibrium are precluded so the concentrations of the final products do increase steadily. The situation is different with intermediates (De Kepper *et al.*, 1982) including autocatalyst species.

- 3) Such coupling among several throughflow systems may bring about instabilities, chemical oscillations which can jeopardize performance of the cleaning system at all: either the reaction may (apparently) stop for some period of time or occur at such levels (with reactants stored and piled up on interfaces of some heterogeneous catalyst involved) that the device can be overheated and thus destroyed by local excess heat production. All “purely chemical” processes and such which involve biological activity, for example, in sewage treatment devices, are subject to this problem, which, in engines, will be aggravated by rapid and abundant changes in power demand and thus altering gas flow rates. The same holds for sewage treatment plants because inputs vary through the daytime in both amount and composition.

All these problems are related to kinetics: besides demonstrating whether the task of chemical purification can be tackled within the volume of a reactor²⁰⁾ in a given period of time, it must likewise be considered whether the reaction does proceed either in a linear rather than oscillatory manner or at least can be controlled by means of chemical engineering. This does determine not just the size of a required purification device (end of pipe reactor) and whether it can be afforded in all financing aspects, matter requirements (e.g., concerning noble metal components of catalytic converters) and energy inputs, but also whether it will or even can be run in some steady-state mode at all. Hence it will not do to identify methods to either withhold a pollutant from the environment or detoxify it by chemical modification (producing less toxic or hardly soluble secondaries) but there are also issues of kinetics beyond reactor size demands: chemical oscillations are but one possible complication, with chemical waves (reaction–diffusion fronts; Pota and Stedman, 1994) observed in CO oxidation at real-life condition-working three-way converters. After its adsorption, CO is oxidized in a reaction front mode²¹⁾ rather than steadily all over the platinum group metals (PGM)-doped ceramic support. This does not matter for a colloquial converter in a Otto engine car (some 50–100 kW) of some 15–20 cm size since the CO oxidation wavefronts are a few millimeters wide and separated by about 1 cm. However, this would be different when cleaning the exhaust gases of a very small (<50 W output, such devices do actually exist, with some 0.2 cm³ stroke volume) model-propelling four- or two-stroke engine. Figure 1.3 shows both the catalyst and the principal pathways of matter flow in a catalytic converter.

Hence the task to estimate appropriate kinetics and energy balances of a plausible process for a possible environmental protection measure cannot be left to

20) Here, a “reactor” can be, for example, some stage of a sewage treatment plant, the three-way catalytic converter in a car, a photolytic apparatus or even some living being, for example, in phytoremediation, extracting heavy metals from soil by plants growing thereon.

21) This does imply that there must be some autocatalyst formed in CO oxidation at the oxide interface. A reasonable candidate for this would be carbonate ion CO₃²⁻, with

carbonates known to be involved in activation of other heterogeneous catalysts for redox activation of small molecules, like that of N₂ and H₂ in the Haber–Bosch ammonia synthesis. There are many wavefront-forming or even oscillatory processes concerning CH acids in liquid-phase chemistry but only one dealing with CO, namely its formation from formic acid (HCOOH)/sulfuric acid (Morgan reaction [Morgan, 1916]).

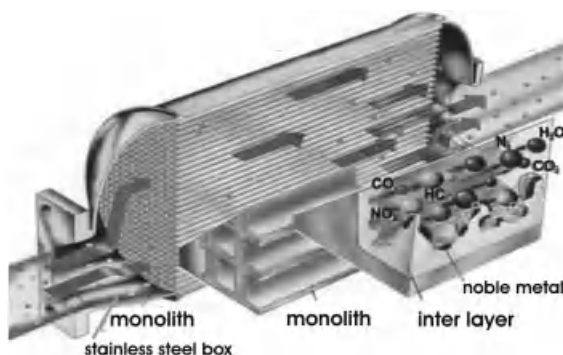


Figure 1.3 A three-way catalytic converter will oxidize both CO and hydrocarbons [all unburned, modified (by thermal partial dehydrogenation, e.g., C_2H_4 or propyne C_3H_4) and secondarily formed ones, like benzene] into CO_2 (and water) while NO_x is reduced into dinitrogen. Here, “monolith” denotes a block of material which is involved in transforming the substrate (exhaust gas), a block rather than a catalyst film covering just the inner surface of a tube. The block need

not be (and actually is not) solid, compact but is porous, with the PGM nanoparticles also covering the inner pores, thus vastly increasing the active surface available for heterogeneous catalysis. The monolith is made from a CeO_x/ZrO_2 (baddeleyite) mixture which absorbs dioxygen (by Ce) and transfers it via platinum group metals to the reducing substrates CO, hydrocarbons (“oxygen spillover”). Photo: Wolfgang Wendt, Berlin.

development engineers but it is more essential: corresponding non-linearities can both preclude up-scaling and down-scaling (like in the fictitious example of fitting a catalytic converter to the silencer of a small or very light model airplane) of a device. Besides, some methods which are successful on a laboratory scale will fail on a larger scale either because corresponding amounts of catalyst components cannot be afforded or because excess heat or by-product expulsion which do not matter on a small scale can no longer be tackled. Once heterogeneities like chemical wavefronts are involved, or retention of process (chemical reaction) heat is required to maintain the system in operation, de-centralized devices for small-scale operations run into trouble, also.

Sometimes, scale-up is precluded just by difficulties of either getting sufficient material or running corresponding larger-scale energy sources.²²⁾ There are examples from all sono-, radio- and photochemistry: although multi-kW sonotrodes are available, their considerable release of low-frequency “waste radiation” (noise, vibrations) renders them awkward to work with—to say the least—while similarly strong radionuclide sources (kW ionizing radiation outputs) are even more difficult to handle for reasons of radiation protection [radioisotope thermoelectric

22) In some cases then substitution is feasible: radioisotope thermoelectric generator (RIG)-sized nuclide radiation sources may be replaced by electron jet sources (Chmielewski *et al.*, 1992; Stiller, 1987)

while the others may be replaced only by some non-coherent light sources (high-power discharge or excimer lamps), if at all.

generators (RIGs), the radiogenic heat production of a lorry-sized Castor container being limited to 40kW] and UV-producing gas lasers (e.g., hydrogen fluoride chemical lasers) for FUV (far ultraviolet; <242nm) or multiphoton photolysis become very large also. Sometimes parameters to run a device can be altered so much as to avoid non-linear behavior. For simple cases—including CO oxidation—limiting conditions for chemical wavefronts or/and (e.g., the Belousov/Zhabotinsky system) oscillations can be determined from theory (e.g., Eiswirth, Freund, and Ross 1991a,b; Eiswirth *et al.*, 1996) but this powerful and efficient method (stoichiometric network analysis) is beyond the scope of this work and also has met but limited practical applications. The more straightforward way to see what happens by changing device dimensions is to link laboratory scale to large-scale apparatus by running a semi-technical scale apparatus.

While environmental chemistry is just concerned with what might be done or with an understanding of natural processes, considering the above dynamic, kinetic and correspondingly technical criteria is required to turn this into “real” technical environmental chemistry or, more generally speaking, environmental technology. Ways to do this and ramifications are discussed near the end of this book, dealing with case studies (Chapter 4).

Apart from this, one must understand the underlying individual processes and their fundamentals, for example, those ruling reaction kinetics at aromatic compounds (Hammett equation; see Section 3.2.3) or redox reactions (redox potential relationships—superposition of Pourbaix diagrams; see Section 3.2.2, Marcus equation) obviously required even to conceive any plausible process, regardless whether it can be scaled up to technical applications at all. All processes are limited with respect to expendable matter and energy flows. The other criterion is borrowed from medicine: Like the oath of Hippocrates demands the doctor not to put additional harm/damage to the patient by his treatment methods (*nihil nocere*), all these processes (the details of which are often poorly understood) must not bring about additional environmental problems. Cases which violate this criterion or principle would, for example, include the production and release of toxic secondaries from some process or the enhanced dispersion of either the original pollutant²³⁾ or some secondary thereof.

How is environmental technology done, then? Now, first of all, environmental methods can either be a reapplication of such procedures which are already established—like in soil remediation where all the strategies of modern mining of low-grade ores or even waste materials are employed in very much the same manner—or the technical solution may be/have been developed for the purpose of cleaning or

23) During the application of chelators (multidentate complex-forming anionic or neutral ligands) to topsoils both for direct extraction of heavy metals and for better performance of phytoremediation measures (plants [and fungi] also make use of chelators such as malic, citric or oxalic acids, certain amino acids, or hydroxamic acids, these moieties

sometimes combined in a single molecule) there also are unwanted kinds or aspects of mobilization: nutrient (cations) may be leached or no longer be bioavailable, pollutants such as Pb, Cd, (excess) Cu, or Be may be mobilized without being completely removed by the plant grown for extraction simply because its rhizosphere is spatially limited.

protecting the environment specifically. Often just some parameters of a given technology or catalyst were adjusted:

- European-style catalytic converters use the very platinum group metals (PGM) alloy of Pt/Rh 5:1 for NO_x removal which was established long before (Ostwald's catalyst) for air oxidation of NH₃ to nitrogen oxide in nitric acid production.
- Hydrogenation splitting of old tyres or plastic wastes into liquid hydrocarbons is done using the same catalytic interfaces as the Fischer–Tropsch hydrogenation of either lignite or hard coal was done for decades at Leuna in Germany (then the German Democratic Republic; GDR) and South Africa, moreover at similar H₂ pressures, temperatures and catalyst compositions.

This alternative just deals with the level of the practical technical approach but not the principal strategy as not a single approach, including techniques from and using biochemistry, is known which was originally designed to improve protection or status of the environment (Fränzle and Fränzle, 2002). For example, fuel cells were a chance discovery, and the arduous attempts by Ostwald and others to use/"burn" coal in high-temperature cells did not deal with environmental protection but with reducing the steps of energy conversion until eventually an electric current is obtained [in addition, these attempts to replace hydrogen or methanol (which must first be prepared) with coal in fuel cell devices were futile]. The case is similar to the direct photocleaning of water [by photocleaning by extreme ultraviolet (EUV), or vacuum ultraviolet (VUV; <200 nm)], removing dissolved xenobiotics at $\lambda \leq 200 \text{ nm}^{24)}$ or photoinduced hydrolysis of halogenated aromatics. The main reason for this would be that technical environmental chemistry and general environmental engineering are far younger issues than the onset of basic research in chemistry, photochemistry and technical physics which in large parts—except for semiconductor and nuclear techniques—can be traced back almost to the very industrial revolution which aggravated those problems later on to be tackled by environmental engineering.

1.3.1

Meaning of Pollutant Degradation

One can alter, modify or degrade chemical compounds considerably but only up (or rather, down) to some well-defined limit. This limit is set by the level of chemical elements, which were defined already long before nuclear techniques were even conceived of, along the following—empirical—rule, dating back to Lavoisier (1780s):

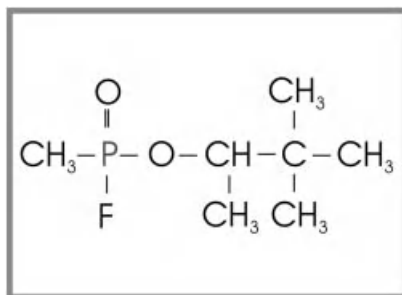
Chemical elements (fundamental radicals, as Lavoisier called them) are "substances which cannot be separated any further by chemical means."

24) Andre Braun and co-workers, Engler-Bunte Institute, Karlsruhe, Germany, personal communication.

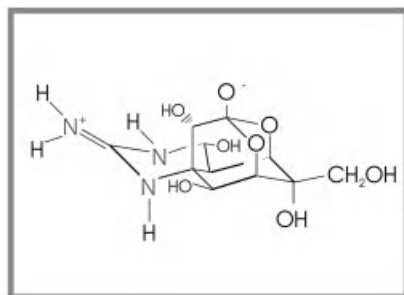
Obviously, this definition does not completely conform to present (after about 1920) knowledge: some electrons can be removed, often rather easily, from a metal atom to produce cations which then are stable in lowly nucleophilic media whereas kinetic isotope effects in chemistry cause some separation (an almost complete one in the hydrogen/deuterium case) among the isotopes of some element during chemical transformation (Preetz, 1969; Krumbiegel, 1986); when, for example, chlorate ClO_3^- is reacted with hydrochloric acid (both isotopically “normal”), the produced (elemental!) chlorine will contain more $^{35}\text{Cl}_2$ rather than ^{35}Cl , ^{37}Cl and $^{37}\text{Cl}_2$ than corresponds to the colloquial 75.4% ^{35}Cl ; 24.6% ^{37}Cl mixture, that is, more than some 57%. Thus some additional separation within an element took place. However, the above definition, although more than 200 years old now, remains to be valid in a way which is most relevant to problems of environmental engineering: regardless of kinds or numbers of chemical or biochemical transformations exerted to the given substance, the atoms of which it is constituted will never “vanish”. It is just possible to bring them into some different chemical bond network, including the elemental state (N_2 , Hg, etc.). This statement holds for all chemical elements, and there is almost no influence of chemical environments on radioactive decay either; and it holds for metals and non-metals alike.

What then is the meaning of the familiar assertion that organic substances, that is, carbon compounds other than carbonates, cyanides, CO, CO_2 or urea, “can be degraded” in either chemical or biological processes whereas heavy metals or their salt complexes cannot? While C or N atoms are as indestructable by chemical means as those of Cd or Ni, we shall soon see that non-metals respond to changes of chemical speciation, be it those of oxidation state, complexation or within covalent structures, with far more pronounced changes of toxicity than are observed in metal compounds or complexes. Toxicological data are often determined with rats (*Rattus norvegicus*), with the toxins being applied in various ways (LD_{50} doses; here: oral). Thus, among F-, Cl-, P- or N compounds toxicity data for simple alkali metal salts of these elements (fluorides, chlorides, phosphates or nitrates, respectively) are compared to action doses of such organic poisons bearing the same elements in a way in which the toxic action can be attributed to the non-metal heteroelement by comparison with closely related compounds lacking this element. The four highly toxic counterparts for F, Cl, N and P, respectively, are: (i) monofluoroacetic acid, which blocks the Krebs cycle mimicking the citrate ion (F), (ii) the notorious dioxin 2,3,7,8-TCDD (Cl), (iii) tetrodotoxin (N), the action of which against the sodium ion channel in nerve cell membranes is caused by the protonated carbamidine function²⁵⁾ (three N atoms) and (iv) the chemical warfare agent soman (GD, the German CW agent D, the isohexyl-2-ester of methylphosphonate fluoride; P; Figure 1.4). While other, more complicated carbamidines such as saxitoxin can be similarly toxic [human lethal dose 1–2 mg (!)] as tetrodotoxin, specific blocking of Na^+ channels is the toxic principle as carbamidines otherwise can very well be dealt with by metabolism; cf. the essential amino acid arginine and its role as a transamination agent in urea biosynthesis (ornithine/

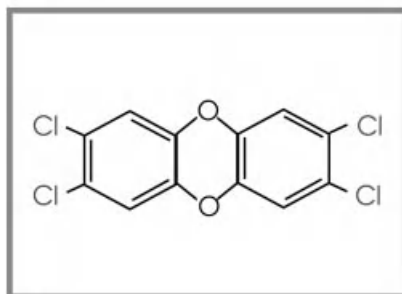
25) To the left in the picture of tetrodotoxin (Figure 1.4).



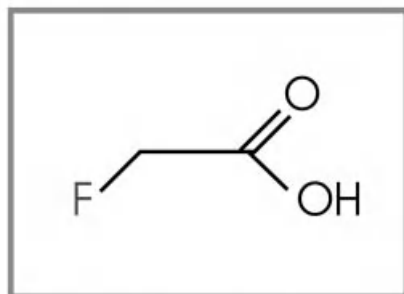
Soman



Tetrodotoxin



TCDD



Monofluoroacetic acid

Figure 1.4 Highly toxic speciation forms of four different non-metals F, Cl, N and P. Pnictogen compounds: soman (GD) and tetrodotoxin. Halogen compounds: TCDD and monofluoroacetic acid.

arginine cycle). Soman and similar phosphonates will phosphorylate serine residues in enzyme acetylcholine esterase much as simple polyphosphates do but in an almost irreversible manner, with a pile-up of acetylcholin in the synaptic area jeopardizing nerve functions once again. These four compounds are found to be relatively much more toxic when compared to the above alkali salts than are different binding/speciation forms of say, mercury or chromium. Allowing for biomethylation or technical applications of arylated or alkylated, hydrolytically stable organometal compounds, the range of toxicities to be covered by different speciation of a given metal or semi-metal (e.g., Bi) might become almost as large as with non-metals, for example, tetraethyltin²⁶⁾ is about 20 000 times as toxic toward rats than SnO₂. Accordingly for metals desalkylation becomes a task in

26) Although it is known as a low-melting metal under ambient conditions, tin does chemically resemble its lower congeners Si and Ge far more than it compares to Pb given, for example, the stability and chemical properties of hydrides (SnH₄, Sn₂H₆), compounds which contain E-E

bonds, oxoanions and so on. Its metal character (>286 K) is limited to the relative vicinity of its 505 K melting point, again like with silicon and germanium, with Sn becoming a small band gap semiconductor below 286 K also, thereby crumbling into covalent crystals ("tin pest").

technical detoxification; usually it is facile to achieve but sometimes matters are different: while tri- or tetraorganotin compounds can be stripped of their alkyl groups by electrochemistry (Stichnothe *et al.*, 2005) readily, the $(\text{CH}_3)_2\text{Tl}^+$ cation will withstand prolonged cooking in 68% nitric acid (Elschenbroich and Salzer, 1988)! In fact, apart from its (likewise enhanced) toxicity (while that of Tl^+ alone is more than considerable) is so stable against oxidation and photolysis that, given the ability of bacteria and fungi to biomethylate Tl (Thayer, 1995), it is difficult to see why there are any speciation forms of thallium other than $(\text{CH}_3)_2\text{Tl}^+$ cation in seawater—and even prevail (Schedlbauer and Heumann, 2000). After all, “heavy metals and their compounds cannot be degraded” really means that “speciation does not matter so much with respect to toxicity than with non-metals (pertinent speciation forms of the latter being almost always covalent and often organic compounds).” In addition, the effects of oxidation states are *inverted*.

In heavy (and some light, e.g., Eu, V) metals higher oxidation states are more toxic (e.g., chromate, Cr^{3+}) than lower ones because oxidized complexes tend to be more stable and thus metals bind more strongly to amino acid side chains and other kinds of biological matter, causing havoc in enzymes whether or not these need metals to operate. In non-metals the situation is different: here reduction means creation of vacant electron pairs at the non-metal site which then readily coordinate to (especially “soft”) metal centers in biomass, which is the mode of action for toxins like CO, CN^- [C(II)], triorganotin *anions* [Sn(II), inorganic As(III)] or trialkylarsines, -stibines, PF_3 . Once the propensity for specific ligand behavior is removed, toxicity does vastly decrease, for example, tertiary arsine oxides (among them many biogenic ones), $\text{As}(\text{CH}_3)_4^+$ and arsenobetaine (also biogenic) are far less toxic than trimethylarsine or similar compounds, NCO^- less than CN^- and so on.

Similar compounds which bear different halogen and pnictogen atoms ($\text{pn} = \text{N}, \text{P}, \text{As}, \text{Sb}, \text{Bi}$, element 115), like bromoacetic acid, brominated or iodinated dioxins or arsonate esters, are far (by several orders of magnitude) less toxic than the four compounds mentioned and depicted above, and the same holds for substances with a differing number of halogen atoms (di-, tri-, heptachlorodibenzodioxins, difluoroacetic acid, etc.). Such organic halogen compounds (or other electrophilic, alkylating agents like oxiranes, aziridines, esters of strong acids like dimethylsulfate), including chloroform CHCl_3 or the above fluoroacetic acid, can add to organic compounds and thus influence biochemistry²⁷⁾ far more than coordination of respective anions to metal centers would do. Soman or TCDD (there are similarly toxic compounds including the heavier halogens, e.g., among bromination products of dimeric cyclopentadiene) are just extreme cases of this effect. However

27) Organic electrophilic agents, like chloroform and ethanol (via formation of ethyl esters, chloroethane in stomach or ethanal CH_3CHO ?) or oxiranes, thus also induce metallothionein (MT) formation by addition to the recognizing sequence of

nucleic acids which then unleashes MT- gene expression. It does not really matter here whether a metal ion does add to this particular strand by coordination or an organic electrophile alkylates it.

also certain non-metals, whether these are susceptible to biological reduction, cannot be “thoroughly detoxified” by appropriate speciation, like boron and sulfur.

These chemical options (principal, among others) can be used for reducing the toxicities and/or solubilities of compounds of different elements:

- A redox process can be used to detoxify some element: Cr(III) is both less toxic and less bioavailable than chromate(VI), which in addition is carcinogenic, whereas As(III) is far more toxic than arsenate(V).²⁸⁾
- Precipitations of sulfides or hydroxides/aquoxides reduce bioavailability to an acceptable extent, allowing the later deposition or other use of the substances (e.g., production of glass, concrete from phosphate precipitates, fly ash, respectively).

While there are various methods to detoxify organic substances by dehalogenation, just a few of them can be applied similarly for the removal of heavy metal wastes (if similar or identical conditions apply for different classes of compounds, fewer steps are required for comprehensive detoxification). However, heavy metals which are rather toxic, at least in some speciation forms, can often be precipitated as pure metals under conditions which otherwise bring about the dehalogenation of organics, that is, the addition of reductants. The majority of heavy metals are distinguished by not-too-low redox potentials [except for rare earth elements (REEs), actinoids]. Conversely, transfer into the elemental state is a viable option for a few non-metals (nitrogen, sulfur, arsenic); but it vastly increases the toxicities of others (halogens). Among attempts for the oxidative²⁹⁾ “destruction” of (mainly organic) pollutants, two principal (yet, sometimes, consecutive) outcomes must be distinguished:

- 1) Degradation of the primary compound, that is, conversion into other compounds containing still element C bonds which are (usually) still oxidizable further—even though this might take drastic conditions, given that, for example, the oxidation of sulfur organics by $\text{HNO}_3/\text{H}_2\text{O}_2$ under pressure and microwave heating does end up at methansulfonate $\text{CH}_3\text{--SO}_3^-$ rather than proceeding into sulfate (Krümmel, 1988).
- 2) Mineralization which converts C and H species entirely to CO_2 and water while other elements (N, halogens) can remain in and be released in some

28) Back in sixteenth century, Paracelsus discussed the already then established method of “improving” the outer appearance of horses going to be sold by feeding them some As compounds. He stated (data given in modern terms/units) that “some 3 g of white arsenic (i.e., As_2O_3) are capable to kill a horse” while “even about 100 g of As compounds (modern terminology) are tolerated if fired with potash in air before giving it to the horse”

(the $\text{K}_2\text{CO}_3/\text{O}_2$ system producing K arsenate[V] K_3AsO_4). Either dose is remarkably high with respect to humans and the man/horse weight ratio.

29) In reductions there is no comparable process, since the C backbones are conserved even though O and halogens (Hal) are cleaved as water and Hal^- , respectively. Some nitrogen compounds, like nitrocompounds, can thus even be increased in toxicity.

reduced form (Cl^- , NH_3) even after the application of drastic oxidation means, like advanced oxidation procedures (AOP).

Often the “efficiencies” of degradation methods are discussed without distinguishing between mineralization and some–limited–restructuring of the primary substance, without even considering toxicological implications of the latter.³⁰⁾ It is commonplace to distinguish between decomposition [x.y% of the original substance have “vanished”, total organic carbon (TOC) is decreased by some amount during treatment] on one hand and by chemical or biological oxygen demands on the other. While the former parameter refers to just a single substance, perhaps one component of a complex pollutant mixture, which is removed to a measurable extent while this afforded products of unknown, possibly larger ecological hazards, with oxygen demands for mineralization essentially unchanged. If atmospheric oxygen—as the terminal electron sink—or at least NO_3^- is not available or just to a very limited extent (lower soil or water layers³¹⁾) this difference between degradation and mineralization becomes the more pronounced although some organisms can mineralize organics almost completely on Fe^{3+} as an oxidant.

Both biological/biochemical processes and others in atmospheric photochemistry—involving far ultraviolet (FUV, <242 nm), OH and NO_2 , NO_3 radicals—are likewise capable to convert rather harmless compounds like ethyl fluoride, 1,1,1-trichloroethane (methyl chloroform) or naphthalene into more toxic ones [here, monofluoroacetic acid, the plant poison trichloroacetic acid, increasing deserted areas in Central Asia, and nitro or nitratonaphthalenes and -naphthols (Pitts *et al.*, 1978; Schauer, Niessner, and Pöschl, 2004, respectively)]. Locusts, mussels and even vertebrates (fishes, frogs) take up and eventually chemically modify xenobiotics, biocides or the products of marine algae and bacterial metabolisms to the extent that they can employ these compounds as poisons against predatory organisms. Here, evolution takes place on time-scales of just decades. Similar effects may also occur in those both poorly defined and highly dynamic consortia of microorganisms which do the job in biological sewage treatment plants.

To give an example, Table 1.2 shows the size of toxicity differences (rather, ratios) for the different speciation forms of 13 elements. This includes

30) Cf. the results of NUV (near ultraviolet ($\lambda = 325\text{--}380\text{ nm}$))/ O_2 photooxidations of polycyclic aromatic hydrocarbons (PAHs), yielding quinones or the photohydrolysis of chloro- or bromoarenes which produce phenols, both being more toxic than the original compounds. Polycyclic quinones formed in the self-sensitized (triplet PAH) O_2 photooxidation of PAHs are bactericidal compounds (obviously detrimental to environmental further degradation) and, besides, toxic (oxidative decoupling) and carcinogenic to metazoans (Brack *et al.*, 2003; Batatineh *et al.*, 2010).

31) If pollutants which can be almost exclusively oxidized by dioxygen are buried in soil and it is undertaken to oxidize them there by pumping air down into deep soil layers by injecting compressed air or H_2O_2 solutions, the oxidation of both sulfide and Fe(II) will onset. One result is a decrease of pH (soil acidification), with several heavy metals put into soluble and mobile states. A deliberate form of this process is bacterial leaching of metals like tin, copper or uranium (cf. Section 4.2.1 on soil remediation methods).

Table 1.2 Toxicity against rats (LD₅₀ oral) for the same element in various binding states.

Element	Class	Weakly toxic	LD ₅₀ (mg/kg)	(mMol/kg)	Strongly toxic	(mg/kg)	(μMol/kg)	Quotient
V	L	VCl ₃	350	2.25	NaVO ₃	98	0.80	2.8
Fe	H	Fe(III) nitrate	3.250	8.0	Fe(II)SO ₄	319	2.100	3.8
Hg	H	Hg ₂ Cl ₂	210	0.9 (Hg)	Hg(NO ₃) ₂	26	80	11
B	N	Na ₂ B ₄ O ₇	2.660	28 (B)	NaBH ₄	69	1.800	16
S	N	K ₂ SO ₄	6.600	38	Thioglycolic acid	73	800	47.5
Cr	H	Cr(III) nitrate	3.250	8.1	K ₂ Cr ₂ O ₇	25	170 (Cr)	48
As	S	Arsenocholine ^{a)}	6.500	39	As ₂ O ₃	10	100 (As)	390
F	N	KF	245	4.2	Na(F-CH ₂ CO ₂)	0.2	2.2	1900
P	N	Na ₂ HPO ₄	12.930	48	Soman	0.4	2.4	12000
Sn	H	SnO ₂	>20.000	>130	Tetraethyl tin	16	70	>18500
N	N	NaNO ₃	1.267	15	Tetrodotoxin	0.005	0.04	375000
Cl	N	NaCl	3.000	51	TCDD	0.001	0.0125 (Cl)	4*10 ⁶

a) Trimethylarsonioethanol cation; [(CH₃)₃As-C₂H₄OH]⁺ gets oxidized to arsenobetaine in the human body also, being highly hydrophilic and subject to renal excretion. For some compounds listed here, for example, dermal or intravenously toxicities are even considerably higher. H = heavy metal, L = light metal, S = semi-metal, N = non-metal. The factor (quotient) given in column 9 relates the toxicity of a given highly poisonous speciation form (column 6) to that of a lowly toxic one (column 3).

organoelement compounds which represent the minimum of toxicity for As³²⁾ while it corresponds to the respective toxicity maxima against rats for Sn, P and Cl. Concerning Fe, Hg (!), Cr and several other elements, organoelement compounds form neither extreme but are intermediate with respect to rat toxicities.

In non-metals, especially their rather complicated compounds like tetrodotoxin (Figure 1.4), attributing the “toxic principle” to a given element (column 1 of Table 1.2) might appear somewhat arbitrary, prompting the following remarks:

- Dioxin toxicity mainly depends on chlorine content and the halogen substitution patterns of the corresponding isomer, making 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD, Figure 1.4) a chlorine compound in its toxic mode of action.
- Fluoroacetic acid (Figure 1.4) and its Na salt, or -esters are more toxic than the other monohaloacetic acids and even than cyanoacetic acid by orders of magnitude.
- In “design” (Schrader’s formula) or nerve chemical warfare (CW) agents, phosphorus may not be replaced by other central atoms producing oxoanions and esters readily (S, As, Cr, etc.).
- Tetrodotoxin,³³⁾ rather than a protein “ultrapoison” like botulinus toxin, is regarded as a specific nitrogen compound because the carbamidinium ion moiety [not the strange arrangement interlinking an octose (!) sugar to a carbonate ester site] is (out-)competing Na⁺ in the sodium channels of some nerve.

Which organisms actually produce tetrodotoxins (all algae, dinoflagellates and marine bacteria are presumed to do so) is still a matter of debate. Anyway, it is accumulated in the livers of bellyfish (*Tetrodo*), in the skins of certain *Dendrobates* and *Phylllobates* poison frogs (which dwell far from any ocean in Central and Southern America!), in some mussels and other mollusks (different parts of the small blue-ring octopus *Atelopus zeleki*) and is used there for either defense or making prey (in the squid mentioned before). Either technical or biological alkylation is capable of altering the toxicities of elements in either direction (though increased toxicity is more common). Exposition of mixtures containing elements

32) As noted before, there is a difference between non-complexing quaternary arsonium salts like arsenocholine (trimethylarsonio)ethanol or As(CH₃)₄⁺ and ternary ones which still act as ligands: “lewisite” CH(Cl)=CH-AsCl₂ is that toxic and irritating, breath-impairing (causing people to tear off their gas masks) that it was abused as a chemical warfare (CW) agent during WW1. Concerning rats, its toxicity is similar to that of As₂O₃. The principal difference is that arsonium salts are rather inert (though possibly lipophilic

in cases like AsPh₄⁺) whereas the three-coordinate As compounds act as ligands, much like CN⁻, CO, PF₃, blocking Fe binding positions while lewisite and similar compounds in addition will react with cystein residues of proteins.

33) Distribution of tetrodotoxin in the 38 different species of bellyfish eaten in Eastern Asia differs strongly, requiring corresponding taxonomical expertise of the cooks who prepare these fish for the frying pan or sushi . . .

which are sensitive to ambient conditions (e.g., reducing media, rich in organics capable of transmitting methyl groups) often allow for biomethylation³⁴⁾ of both metals and non-metals. This can thus either increase or decrease the toxic risks of the above mixture [Challenger's or Feldmann's experimental setups (Challenger, 1945; Feldmann and Cullen, 1997)]. The same holds for oxidating conditions, depending on the presence of certain elements. Hence, analysis of the composition of, for example, a superfund site is essential before doing any change to the internal conditions. Oxidized forms are more toxic in V, Hg, and Cr, less so in Fe and As. Relative toxicity changes increase in the order: vanadium (III; V) < iron (II; III) < mercury (I; II) < chromium (III; IV). The toxicity of a metal-organic compound, chromium hexacarbonyl, $\text{Cr}(\text{CO})_6$, [$\text{Cr}(0)$, $\text{LD}_{50} = 1.05 \text{ mmol} = 230 \text{ mg/kg rat}$] lies between the toxicities of soluble $\text{Cr}(\text{III})$ and chromate.

For carbon or chlorine compounds, it is possible to alter toxicity values by changing the binding networks to an outright dramatic extent by, respectively, up to six or 11 orders of magnitude. For "heavy metals",³⁵⁾ this possibility is much less pronounced. The term "heavy metals" (introduced back in 1904) to denote certain toxicological—rather than just chemical—features now is mainly considered outdated for reasons of indeterminate, if not arbitrary use; many even recommend to omit it altogether. However, for example, Fränzle and Fränzle (2002) identified those common features in terms of quantum chemistry which cause "softness", thiophilic behavior, pronounced tendencies for complex formation and also high toxicity of so-called heavy metals all alike. Among these, chromates(VI) and trivalent Cr salts differ by some factor of 50 (1.7 orders of magnitude), only, for other metals the differences among toxicities of speciation forms are even smaller. The larger effects for Hg and Cr are not related to the formation of covalent compounds like CrO_4^{2-} oxoanion or the Hg_2^{2+} clusters chemically differing from rather ionic

34) Introduction of other alkyl or even aryl groups than CH_3 , including ones which bear additional functional groups ($-\text{OH}$ in arsenocholin, arsenosugars, $-\text{COOH}$ in arsenolipids) is apparently limited to As and Hg, while binary hydrides (rather than alkyls) are formed by biology with even less elements than methyls are (not with Se, Te, Sb, Bi, Ge), plus PH_3 . Hence, it is justified to call the process simply biomethylation and estimate the effect of binary alkyls (the neutral polymethyl ones not being formed with elements such as Tl, Sn, Pb, Au or Pt) using data on methyl compound toxicities.

35) A simple comparison of chemical properties along groups of the periodic system of elements (PSE) actually reveals that chemical features of "light metals"—sulfides undergoing ready, if not vigorous, hydrolysis rather than being precipitated from aqueous solutions (Al,

Ga vs In), violent reactions of metal alkyls with both air and water rather than their formation by biomethylation in aqueous media (Al vs Tl)—can be related to one limiting value of metal density, which is 6.0 g/cm^3 . The heavy alkaline earths Ba and Ra (which are below this limit) behave much like their lighter congeners Ca and Sr, while V differs considerably from Nb and Ta; and Eu ($\rho_{\text{metal}} = 5.26 \text{ g/cm}^3$) differs considerably from all the other rare earth elements (REE), as do Sc, Y from La, REE (except Eu) and Ac. Considering the fact that quite often much lower "threshold densities" are introduced in an obviously quite arbitrary way (5.0 or even 4.5 g/cm^3), without actually considering the above facts quite well-known to both inorganic, bio-inorganic chemists and toxicologists, the term should no longer be used unless giving a working definition like this before.

species: Hg(II) compounds like HgCl_2 are not ionic either – used as non-electrolytes in aqueous or similar donor solutions (Waddington, 1972; Cotton and Wilkinson, 1981) – and Cr(III) forms complexes readily which are kinetically fairly inert although not very stable in absolute thermodynamic terms. Remarkably, fluoro-complexes – including those which will not undergo hydrolysis *in vivo*³⁶⁾ – are considerably more toxic than both other speciation forms of the same element or fluorides of Na, K.

Reconsidering heavy metals, effects are superposed which include:

- Substitution/removal of physiologically present and active metal ions from proteins, where they are labily bound (see Fränzle 2010 for the reasons of this) – for example, of Zn by Cd or of Fe by group 13 metals Ga or In, often causing
- Blockade of active centers, which also occurs when thiolate groups react with heavy metals M^{2+} (e.g., $\text{M} = \text{Cd}, \text{Hg}, \text{or Pb}$), alcohols or phenols, serine, threonine or tyrosine residues react with Ti(IV), precluding their functional control (“switching on or off”) by phosphorylation, eventually
- Differences in resorption efficiency and sites of possible accumulation owing to unlike speciation: along the sulfate carrier, chromate gets transported all the way into cellular nuclei where it oxidizes nucleic acids (Wetterhahn and Hamilton, 1989), amino acids and sugars, being retained as Cr(III) then, while just a few percent of original Cr(III)³⁷⁾ become resorbed (Figure 1.5, modified after Kaim and Schwederski, 1991).

In environmental technology, the treatment of xenobiotic compounds is considered successful when some combination of the following effects is achieved:

- Acute (short-term) detoxification;
- For organic and element-organic target materials, chemical oxygen demand (COD) and biochemical oxygen demand (BOD) values approach zero after

36) At least as far as can be guessed by lack of fluoride necrosis in tissues. Human serum, for example, is highly aggressive toward covalent fluorocompounds, readily destroying polytetrafluoroethylene (PTFE) interfaces (hence, PTFE cannot be used to cover the interfaces of artificial joints in humans or other mammals) and rendering fluoroacetate, S_2F_{10} , extremely toxic. Possibly this also holds for fluorocomplexes of metals like Al, Fe and rare earth elements. A notable exception among fluorocarbon compounds or functional groups is the CF_3 group which can be produced by some unidentified marine organisms apparently (presence of substantial CF_3COO^- in parts of the deep ocean not accessed by CFHC downmixing yet; Frank *et al.*, 2002). CF_3 functions as

such are no subject to biodegradation (cf. fluoroorganics like halothan, perfluorated tributylamine, R134a, or R113) or to electro- or nucleophilic attack.

Correspondingly trifluoromethyl groups are often introduced in pharmaceuticals for enhanced stability, such as with fluoxetine (ProzacTM), which is a β -phenethylamine antidepressant agent with a para-trifluorotolyl ($4\text{-CF}_3\text{-C}_6\text{H}_4\text{-}$) group.

37) Among the metals mentioned here, Cd was proven essential and involved in enzyme function of certain algae (*Thalassiosira* spp. [Strasdeit, 2001]), with mammal (goat) essentiality also likely at least (Anke, Groppe and Schmidt, 1987; Memiši *et al.*, 2008), while essentiality of Cr for animals including man is now considered unlikely (Stearns, 2000).

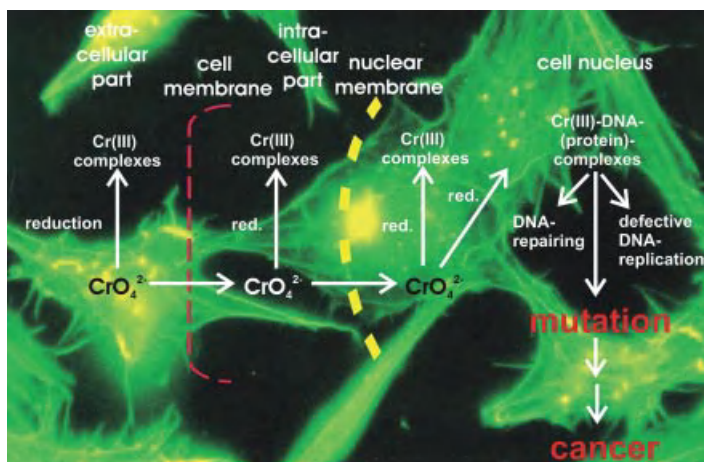


Figure 1.5 A schematic representation of uptake and reduction of chromate, linked to its mutagenic activity inside cells (courtesy of underlying photograph: Prof. Barnekow, Department of Experimental Tumor Biology, Münster, Germany; scheme overlaid by the authors).

treatment, excluding uncontrolled remobilization or retoxification of materials in either aerobic and anaerobic conditions, more generally speaking;

- Production of speciation forms which are “green” or compatible with environment for long periods of time (non-toxic, inert, insoluble or at least incapable of harming environment by subsequent reactions which produce secondaries relevant to, e.g., climate change or atmospheric chemistry).

With phosphorus, tin, fluorine or chlorine—other than arsenic—a comparison among toxicities of “organic” and inorganic (mainly, salt anion) binding/speciation forms of these elements shows that destruction of element-carbon (E-C) bonds will cause considerable decreases of toxicity: phosphate or phosphonate esters, including both “agrarial” biocides and chemical warfare (nerve) agents, fluoroacetic acid, polychlorinated dioxins, -dibenzofuranes and di-, tri- or tetraorganotin compounds are so much more toxic than inorganic halides or phosphates or SnO_2 , that it really does not matter how mineralization (i.e., complete degradation of E-C bonds) is achieved. Some practical options for the above purposes include:

- Reductive dehalogenation;
- Electrochemical oxidation (Sn and Pb organyls, halophenols), including catalysts like $\text{Ag}^{+/2+}$ (dissolved, P-based CW agent cleavage);
- Hydrolysis of haloaromatics using UV radiation, producing corresponding phenols;
- Cleavage of organohalogens in conditions of silent-discharge oxidation (combustion by OH radicals or electrochemical reduction; Kopinke *et al.*, 2000);

- Photoelectrochemistry (oxidative and reductive processes at the same, photoexcited semiconductor; Fränze, 1996; Kokorakis *et al.*, 2000; Fränze *et al.*, 2010) in a system which consists of a colored oxidizing metal complex adsorbed to a broad-gap semiconductor;
- High-temperature hydrolysis and oxidation (“fluid combustion”) in supercritical water vapor.

These methods are discussed in more detail later, so here it suffices just to describe the basics:

- 1) Halide ions can be removed from C-Hal ($\neq$ C-F-) bonds readily by electrochemical means (cathodic reduction), solvated electrons in liquid NH_3 , amines or by heating with appropriate reductants like solid/molten sodium oxalate.
- 2) Organotins may be oxidized to SnO_2 hydrate and the corresponding alcohols at an anode (Stichnothe *et al.*, 2005). Catalytic varieties (Weinberg and Weinberg, 1968; Kyriacou, 1994) include anodic formation of reagents like Ag^{2+} , $\text{Co}^{3+}_{\text{aq}}$, Ir(V) —attached to the interface—which, although short-lived in water themselves,³⁸⁾ react so much faster with the corresponding pollutants, including phosphonic chemical warfare (CW) agents in the silver system (Emsley, 2001), that the latter can be cleaved, abstracting halogens other than F in the same turn.
- 3) Aromatic and some aliphatic organohalogens undergo *hydrolysis when exposed to UV radiation* in aqueous solution or suspension. This even is used in UV dosimetry, with quantum yield $\Phi \approx 1$ for chloride formation from ClCH_2CO_2 ⁻³⁹⁾ at $\lambda = 254\text{ nm}$ (Becker *et al.*, 1991) whereas chloro- or bromobenzenes form phenols and Hal^- ions. Nitrocompounds can undergo both nitrite cleavage (in the same manner) or intramolecular photooxidations. Haloarene photohydrolysis, however, is a critical feature especially when it occurs with $\lambda \geq 300\text{ nm}$ in halo-PAHs: while glycolate is much less toxic than chloroacetate, quite the opposite holds for chlorinated or brominated benzenes and toluenes: in the rat (oral application), ortho-methylphenol (2-cresol) is about 40 times more toxic than 2-chlorotoluene. Moreover and even worse, chlorinated dioxins will form from the familiar though out-phased polychlorinated biphenyls (PCBs) upon irradiation.

38) The corresponding redox potentials of these ions are about +2 V vs normal hydrogen electrode (NHE; $\text{pH} = 0$), so there is just kinetic preference against oxidation of water which is present in large excess, of course. Ag^{2+} even is capable of oxidizing O_2 and xenon in cold, acidic, non-aqueous and non-oxidizable fluorophoric solutions (Klapötke and Tornieporth-Oetting, 1995)!

39) Note that here the carboxylate anion undergoes photocleavage of some substituent whereas “unsubstituted” carboxylates do not undergo any photoreactions (only neutral R-COOH undergo loss of CO_2 or CO_2H radicals [Mittal, Mittal and Hayon, 1973] at somewhat shorter wavelengths).

- 4) Another way toward mineralization of organic pollutants is their *combustion*. Dioxines and dibenzofuranes—like chlorofluorohydrocarbon (CFHC)—undergo complete destruction if in contact with red-hot carbon, that is, by co-combustion in a coal-power plant, leaving behind only CO₂, water and alkali or alkaline earth halides.
- 5) *Photoelectrochemistry*—in its classical way—provides a combination of oxidative and reductive processes.⁴⁰⁾ Concerning environmental chemistry, all mineralization of various kinds of organic contaminants, detoxification of alkylmetal compounds by R cleavage and of As(III) by oxidation were demonstrated. Some toxic noble metals can be removed from solutions by photoelectrochemical cementation (precipitation of pure metal like with Cu, Ag, or Pd).
- 6) “*Fluid combustion*” is achieved using supercritical water vapor at $p \approx 300$ bar and temperatures of 400–650 °C. Under these conditions, beyond the critical data of water, water is a gas and thus miscible with every other gas, including dioxygen, but, being almost as dense as a liquid owing to the high pressure,⁴¹⁾ produces considerable solvation, taking up unpolar organics, also. The rates of hydrolysis of, for example, esters or amides become very large, with dioxygen causing oxidations (except for the upper end of the temperature range, where direct oxidation of CH₄ and higher hydrocarbons by water according to $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3 \text{H}_2$ etc. does not occur⁴²⁾).

Methods which draw upon redox processes meet the common difficulty that there is no linear or even only parallel relationship between redox potential and toxicity of produced speciation forms among different elements, with mixtures of pollutants quite common in practical cases. Hence trying to produce some extreme value of redox potential—either oxidizing (anode, but also with water chlorination) or

- 40) Of course, cross band gap excitation produces equal numbers of conduction band electrons and valence band holes (where electrons are missing) in any semiconductor, regardless of its chemical identity and possible doping, just for reasons of charge conservation. As long as the semiconductor is stable, not undergoing photocorrosion, both kinds of charge carriers will eventually turn up at some outer interface of the particle and react with substrates there. However, the speed of charge propagation depends on semiconductor and doping, being equal only in few materials (e.g., undoped elemental germanium, AlP or AlAs). The problem of unwanted electron reactions can be resolved by relocating light absorption and hole production into some sorbate layer made of metal complexes (Fränzele, 1996; Kokorakis *et al.*, 2000).
- 41) At T_c and p_c , solvents have about one-third of their ambient-conditions density. In a colloquial supercritical system, the temperature is not much higher than T_c , but the pressure usually exceeds p_c considerably. Hence the density will be $>1/3 \rho_{\text{normal}}$, and hence there is considerable solvation, but no dissolution of common salts as supercritical solvents are unpolar solvents. However, this allows the mixing of long-chain hydrocarbons and O₂ in water for “fluid combustion”.
- 42) Amino acids other than glycine, alcohols and so on do not decompose in hot water already much below the critical point producing H₂, carbon oxides, carboxylic acids and NH₃ (Schulte, 1999).

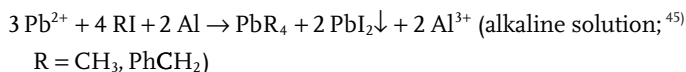
reducing (cathode with large hydrogen overpotential, solvated electrons in liquid NH_3 , amines) –, be it by “purely” chemical means, electro-, photoelectro- or even radiochemistry (production of hydrated electrons, conversion of these into OH radicals⁴³⁾), will include some risk of producing highly toxic intermediates from some components of the pollutant mixtures even when detoxifying most of the others. If so, intermediates must be kept safely from escaping the reaction chamber of remediation. Otherwise, the (frequent) case of mixed contaminations, for example, a mixture of As(III) or organotins with heavy-metal compounds (the toxicity of which increases upon oxidation of the mixture) calls for a secondary or even multi-step treatment of the reaction mixture.

By superposition of the Pourbaix diagrams for the corresponding elements and their toxicological data, some “window” of acceptable compromise conditions can be identified for the purpose of both immobilization and detoxification. One-step clean-up can only be achieved if the optimal speciation forms will stably coexist. For example, in the wastewaters from leather-making and dyeing, which (at least in earlier times) used to combine chromate with residues of As, Ni and other elements, it is necessary to ensure complete reduction of CrO_4^{2-} without reducing AsO_4^{3-} by an appropriate redox potential, unless the redox potential is taken so far down as to produce elemental As.

Whereas organotins react readily at anodes (Stichnothe *et al.*, 2005), certain other element–carbon bonds (e.g., bonding to As, Tl, Hg, Si or F) may be both toxicologically relevant and highly stable, even allowing for extreme redox potentials and/or attack by chemicals like concentrated nitric acid.⁴⁴⁾ Such compounds can be readily formed by both fungi (moulds, in particular) and various microorganisms; besides, bioalkylation of certain elements was also detected in mammals (for man, e.g., As and Bi; Hollmann *et al.*, 2010) and Hg^{2+} can formally abstract R^- (carbanions) from many organoelement compounds including silicones, producing extremely toxic RHg^+ ions. The familiar light-metal technical materials themselves form only organometals which violently hydrolyze and react with air. Nevertheless, in aqueous environments, they (e.g., Al) can bring about formations of the hydrolytically stable but more toxic organometals (e.g., lead tetraalkyls) from metal salts and organohalogens in some cases (Ahmad *et al.*, 1980):

- 43) 1) radiolysis of water: $\text{H}_2\text{O} + \gamma \rightarrow \text{H} + \text{OH}$, then (in alkaline solution)
 2a) $\text{H} + \text{OH}^- \rightarrow \text{e}^-_{\text{aq}} + \text{H}_2\text{O}$
 2b) $\text{N}_2\text{O} + \text{e}^-_{\text{aq}} \rightarrow \text{N}_2 + \text{OH}$ or (in acidic solution)
 3) $\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{OH}$
- 44) Concerning As, trimethyl arsane (Gosio gas) in the atmosphere is not mineralized into inorganic As in the atmosphere and hydrometeors, notwithstanding the joint attack of UV radiation and OH radicals; rather the dominant As compound in

rainwater is cacodylic acid (dimethylarsinate), having lost just one CH_3 group. Concerning thallium, the $(\text{CH}_3)_2\text{Tl}^+$ cation (Schedlbauer and Heumann, 2000), which can be produced by certain bacteria (Thayer, 1995), is so stable toward both UV and even prolonged boiling in 70% nitric acid (!) (Elschenbroich and Salzer, 1988), that it is hard to explain why there are any other speciation forms of Tl in the ocean, actually.

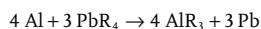
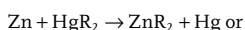


To understand these non-linear changes of toxicity experienced when changing ambient redox potentials and how to deal with them, consider the above example + nitrogen as cuts through the Pourbaix diagrams at constant pH = 7.5. The rodent toxicity of the inorganic speciation forms of N, Cr, and As all vary upon changes of their redox potential (Figure 1.6).

In systems dynamics, concerning both mechanical and chemical systems with some feedback features, for example, in the double pendulum, in celestial mechanics (feedback by mutual gravity attraction) or in chemical oscillators (feedback by autocatalysis of formation of some reaction intermediate), oscillatory, pendulum-like behavior—also suggested to occur in population dynamics—will not simply impose some periodic or quasi-periodic perturbation on otherwise linear kinetics to produce a sine-like modulated linear process. Rather, something quite different will happen: chaos (May, 1976); in fact, chaos was first noticed to occur in celestial mechanics (by Laplace—already around 1800!). In deterministic chaos, deviation from the predicted, unperturbed trajectory increases with time in an exponential manner which is neither predictable nor reproducible in repeated runs of the experiment (e.g., a planetoid subjected to chaotic track perturbation by the interaction of, with and among several larger bodies may appear anywhere in the Solar System or may get ejected altogether), chemical oscillators, rather than producing periodic changes of state variables (pH, redox potential, optical spectra) over few or even hundreds of cycles, then lose any foreseeable kinetics after initial period doubling.⁴⁶⁾ Chaos accordingly refers to apparently erratic, unpredictable changes of concentrations or abundances of certain actors involved in the system—even biological species—and correspondingly of kinetics (as the latter refers to the consumption or production of some intermediate species. For some period of time, it was outright fashionable to attribute features of deterministic chaos to quite diverse kinds of systems with any mode of feedback involved: non-periodic mass

45) This reaction is remarkable for at least three reasons:

- 1) Organoaluminum compounds forming from Al and RI spontaneously ignite in air and violently hydrolyze.
- 2) As was already discovered by Edward Frankland (1825–1899) in the 1850s, in some inert solvent, mixtures of alkyls or aryls of rather noble metals, for example, Hg, Cu but also Pb, react with metallic Al or Zn or Mg exactly like halides of the above more “noble” elements would do, thus destroying the products which are found to be stable here (i.e., in water), for example,



- 3) Organolead compounds are extremely neurotoxic (this is the reason for ecological relevance).
- 46) These are no oscillations around chemical equilibrium; the final approach of some chemical oscillator toward equilibrium occurs in a classical, linear manner in every case. “Real” chemical chaos yet is rare, requiring multiple feedback modes like those possible in oxidations of thiocyanate ion ($\rightarrow \text{HSO}_4^- + \text{HCN}$), the paradigmatic system being the ClO_2^- chlorite-based oscillator which oxidizes SCN^- (Doona and Doumbouya, 1994), $\text{S}_2\text{O}_3^{2-}$ or thiourea.

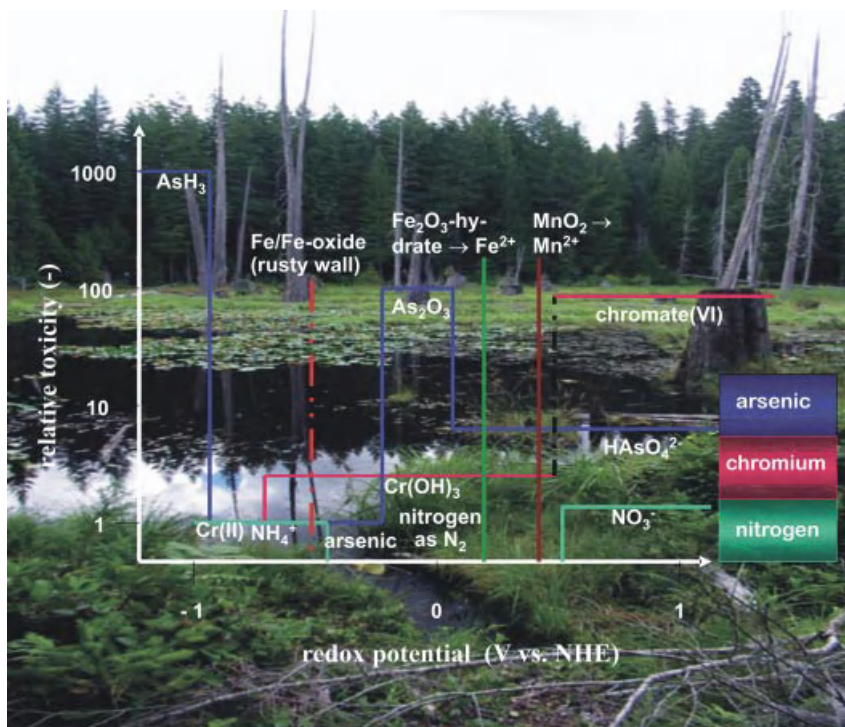


Figure 1.6 Dependence of relative (rodent, oral) toxicities of three elements N, Cr, and As of redox potential of soil or groundwater. A “rusty wall” made from iron (Fe filings dispersed by sand or gravel) accordingly is

best suited to minimize the toxicities of all three elements (background photograph courtesy of Wind River Company Crane Research Facility, USA; scheme overlaid by the authors).

abundances of migratory locusts or of lemming voles were interpreted as signs of chaos, and so were apparent breakdown of some catalytic chemical systems, stock-exchange crashes and many others. Concerning environmental technology, chaos appears both in certain, additionally photochemically perturbed reaction sequences and in technical oscillations. Chaotic dynamics of populations—if they actually exist—would pose some severe problems in biotechnological plants of various kinds, for example, for sewage treatment or bioremediation.

When analyzing or designing some device of environmental technology and its modes of operation, quite a number of different approaches are at hand. They are not only grossly different with respect to complexity of comprehension (somewhat alleviated by the option to use standard modeling software for chemical engineering nowadays—perhaps without really understanding what you are doing . . .), but also concerning the “response” of the modeling procedure toward the reduction of complexity: if you omit some features or leave aside some partners of a feedback loop, can you still make sure (by some general mathematical proof) that the model you chose to use will reproduce the actually observed dynamics, exotic as they

might be? Maintaining the principal behavior, for example, oscillations or exponential growth, in this “reduced” model obviously *suggests* you conserved the features and subsystems which are in charge of “exotic” dynamics but you still have to give proof that this assumption actually applies.

Some of these models, extracting features of autocatalysis combined with the topology and sign (negative, positive) of feedback loops from a “background” of “boring” linear processes (stoichiometric network analysis, SNA; Clarke, 1974, 1980; Eiswirth, Freund, and Ross, 1991a,b) were used by these authors (Fränzle and Markert, 2000a,b, 2002a,b, 2003, 2007; Fränzle, 2010) to work out the results of autocatalysis (in biology, reproduction) from the background of other events in metabolism or even in entire biocoenoses or ecosystems. An advantage is their sometimes more straightforward approach into complicated feedback dynamics, as compared to classical computer simulations of feedback. Even if this is “open-source” code, the interested colleagues—and more so decision-makers and stakeholders—must rely on (in effect, just believe in) the correct implementation of the corresponding assumptions in the code (but this cautionary remark also holds for simulations in architecture statics or aircraft aerodynamics!). Yet, qualitative arguments from SNA—which is by no means restricted to chemical or biochemical systems, but also applies to nuclear fission energy, astrophysics and other topics (Clarke, 1980)—were successfully used both in ecological planning and in understanding long-term large-scale dynamics in economy (Kondratieff-type long waves; Grossmann *et al.*, 1997; Fränzle and Grossmann, 1998).

When looking for possible causes of identical kinds of damage to the biota, such as chlorosis in green plants, it still remains difficult to obtain sufficient pieces of information for pinpointing the actual cause of some problem: when some species x (plant or animal, etc.) in some forest area y rapidly declines in number, what is this due to? Is it the impact of heavy metal a , herbicide b , virus c [such as both Ebola and simian immunodeficiency virus (SIV, causing AIDS in apes) in the decline of the great apes in Central Africa], some predator d which was released there or immigrated in unusual conditions (such as wolves passing the ice cover of the Great Lakes in 1948 to invade an island which hitherto had been a riskless though overused habitat for thousands of mooses, reducing the latter to some 25 at first) or is it due to “bad weather” (e , which may introduce geochemical consequences also), rather than “bad luck” in the realm of chaotic dynamics? Five variables in this example (a – e ; counting heavy metals and viruses as one single cause each, which is obviously oversimplified) demand five independent investigations—difficult enough to get in field studies—varying one parameter only per study. Even then, you end up with mathematically meaningful statements on just one species and its responses, one of very many which interact⁴⁷⁾ in a biocenosis.

47) Cf. the experiments on population dynamics in small temperate lakes in Canada (Sterner and Elser, 2002): (i) removing all the top-level piscivorous predators by fishing, exclusion (fences) of bears or otters, (ii) adding certain chemicals or (iii) manipulating the C/N/P ratios of dissolved and particulate organic

matter suspended in these water bodies and investigating the effects on populations of zooplankton and planktivorous fishes. Some of the latter effects are both seemingly paradoxical and hard to distinguish from each other, making causal analysis in real-life systems next to impossible.

When you eventually cast your assumptions or empirical “if–then” statements on the systems and its dynamics (population, chemical, etc.) into a model using partial differential equations to study the dynamics, you end up with systems of coupled equations which can only be solved when there are *at least as many* independent equations (with each one representing one fully characterized experiment or field study) as there are different variables (five in our oversimplified example). Accordingly, except when looking for the specific inhibition of porphyrin biosynthesis, the analytical determination of, for example, Pb in some biocenosis or biogenic sample thus tells you almost nothing, let alone the question whether this lead is excluded from bioresorption by being precipitated as sulfide (galenite), sulfate, chlorophosphate or carbonate in the sediment, or becomes both lipophilic and neurotoxic by bio- or anthropogenic alkylations. *Speciation*, of course, is a chemical criterion. Metal ions, for example, might occur as mixed-oxide particles, aqua- or ligated complexes, bound to dissolved organic matter (DOM), biomass and in other forms. A classical hypothesis (Shaw, 1961; Bienvenu, Nofre, and Cier, 1963) which also made its way into ecotoxicology (Lewis *et al.*, 1999; biotic ligand model; Santore *et al.*, 2001; Paquin *et al.*, 2003) postulates the critical property of a “cocktail” of metal speciation forms around some organism to be the concentration (or, rather, chemical activity) of the “free”, that is, aquated ion. This assumption, called the free ion activity hypothesis (FIAH), was derived by noticing that simple salts or labile complexes of metals are⁴⁸⁾ much more toxic than stable complexes containing the same metal ion. According to FIAH, it is the free ions which interfere with metabolism, for example, by replacing essential metal ions in metalloproteins or reacting with disulfide bridges to destroy protein tertiary structures. In some stable complexes, like hexacyanocobaltate, it is almost impossible to cleave the “shroud” of cyanide ions to uncover the $\text{Co}^{3+;2+}$ ion which thereafter could become toxic. Unless the very ligands are used or else degraded by biomass itself, this barrier would hardly be passed. Part of the difficulties met by FIAH are due to the often pronounced changes of relative stabilities of various complexes when the metal centers undergo redox reactions.

1.3.2

Substances and Their Sources

Chemically most diverse substances get into the three environmental compartments air, water and soil steadily. Possible sources include biological, geological (erosion, weathering, volcanoes) and other natural events such as forest wildfires but also—to a substantial extent—human activities like agriculture, industrial activities or traffic. Natural and anthropogenic trace gases and their respective sources are discussed in more detail in Section 2.2.1. If the compounds passed into the environment do not undergo fast chemical

48) There are different exceptions to this empirical rule, mostly with respect to the uncommon oxidation states of some metals, like the extreme toxicity of neutral

metal carbonyls like $[\text{Ni}(\text{CO})_4]$, or the toxicity problems associated with fluorocomplexes, including very stable ones.

changes,⁴⁹⁾ they undergo transport and distribution/partition among the environmental compartments. Otherwise, if there is high reactivity and hence a short lifetime of the primary substance, the above statement will likely hold for their long(er)-lived reaction products.

What does promote corresponding reactions? The principal driving force for both transport and partition of the chemical inside and among environmental compartments are chemical gradients, including those of temperature as well as pH differences among some water bodies and the underlying or surrounding sediments. These may influence the partition of both acidic and alkaline species, including metal ions. Even if the corresponding gradients are absent, partition will take place due to adsorption or similar equilibria when particles get bound (adsorbed) to particles and then transported or deposited in this solid state. Substances listed in Table 1.3 can be grouped, for example, according to:

- Volatility;
- Tendency to change or be moved into some other environmental compartment than that they were produced or released in(to). A further criterion for grouping considered in Table 1.3 is:
- Persistence.

As a rule, inorganic, degradable and persistent organic compounds are distinguished. Of course, the difference among the latter two is quantitative rather than qualitative, floating and subject to definition; in addition, inorganic gases and anions (may) also undergo oxidative or biological degradation or bind to soil components in an irreversible manner by, for example, complex formation. For example, both ammonia and cyanide are processed by certain organisms (nitrification, i.e., NH_4^+ oxidation eventually to yield NO_3^-) even though they are toxic for most others and many excrete them. NH_3 , SO_2 and CO are too short-lived (weeks to few months in troposphere) to undergo global transport, which means their transport ranges are limited rather than global. Like organic compounds, heavy and light metals can be partitioned into all environmental compartments and biomass.

After being emitted into one environmental compartment, substances undergo partition among the three compartments according to their chemical properties. Salts, for example, will (possible, at most) dissolve in water or groundwater, while aerial transport is feasible in aerosol only. Volatile organic compounds are readily moved by wind but get strongly adsorbed to soil, while their behavior in water is

49) "Not undergoing chemical changes" here allows for reversible processes through, for example, the dissociation of (volatile) organic or inorganic acids when dissolved in water. Although acetic acid (partly) dissociates in water, it can be distilled from aqueous solution when and because it can return into a molecular, volatile state due to the acid/base equilibrium (formic

acid, HCOOH , a considerably stronger acid than CH_3COOH , also is a component of the [mainly polluted] atmosphere which is in equilibrium between the gas phase and rain drops, and the same holds for HCl , HNO_3 , although these display far more dissociation in aqueous solutions [gas phase levels of all three: ≈ 1 ppbv]).

Table 1.3 Kinds of pollution and pollutants in the different environmental compartments (from Markert and Friese, 2000, with modifications from Förstner, 1995).

Environmental compartment	Bound substances	Examples	Source(s)
Water	Degradable organic compounds	Fecal matter, tensides, solvents, pesticides, chemicals used in technical processes, fats, oils, soluble residues from plant or animal origins, fundamental chemicals, intermediates and terminal products	Town, villages, domestic uses, agriculture, textile processing, metallurgy, painters, food, chemical and paper industries, waste dumps
	Persistent organic compounds	Tensides, solutions, pesticides, commercial chemicals, basic chemicals, intermediates and terminal chemical products	Agriculture, textile processing, metallurgy, painters, chemical and paper industries, waste dumps
	Inorganic compounds	Heavy metals, salts, cyanides, chromates, fertilizers	Metallurgy, metal huts, leather production, towns and settlements, agriculture, waste dumps
Soil, sediments	Degradable organic compounds	Fecal matter, pesticides, residues from plant or animal origins, fundamental chemicals, chemicals used in technical processes, intermediates and terminal products, sewage sludge	Agriculture, domestic and toxic waste dumps, waste disposal facilities
	Persistent organic compounds	Tensides, solvents, pesticides, commercial chemicals, fundamental chemicals, intermediates and terminal chemical products	Toxic and industrial waste dumps
	Inorganic compounds	Heavy metal compounds, salts, ashes, sludges	Waste dumps, waste incineration facilities, metal production
Air	Organic gases	Solvents, hydrocarbons, volatile pesticides, volatiles from industrial chemistry	Painters, refineries, agri- and aquaculture
	Inorganic gases	Carbon monoxide, hydrogen chloride, sulfuric acid, nitrogen oxides, ozone, metal vapors, carbon dioxide, ammonia	Combustion chambers, incineration plants, engines, industry, NH ₃ , also from agriculture
	Dust(s) and smoke	Metal oxides, PAHs, soot	Metal production, waste incineration, combustion plants in general

dictated by both (aqueous⁵⁰⁾) solubility and adsorption tendencies. The quantitative relationship is given by partition coefficients, for example:

$$K_{\text{sediment/water}} = \log\{C_{[\text{substance in sediment}]} / C_{[\text{substance in H}_2\text{O}]}\} \text{ (equilibrium assumption)}$$

One must distinguish three different scenarios, namely:

- 1) Enrichment/accumulation in sediment,
- 2) Comparable shares of compound in either environmental compartment and finally, the opposite, that is:
- 3) Extraction of something from aquatic sediment into the water column above it.

The latter is likely when some river or wind-agitated standing water body uncovers sediment layers which took up pollutants long before by erosion or when compounds are passed into water which participate in extraction by, for example, complex formation [with a ligand like ethylenediaminetetraacetic acid (EDTA) being added, see also Section 4.2.2] or nonpolar liquids spilled into water. Of course, partition coefficients depend not only on the composition of the solid phase but also on the properties of water such as pH (the distribution/partition of anions of longer-chain carboxylic acids or of phenols differs considerably from that of neutral compounds), ionic strength or the presence of tensides (including biogenic ones like certain fragments of cells or lecithine). Yet there are empirical relationships to $\log k_{\text{OW}}$, permitting an extrapolation from known behaviors of few substances in a water/sediment biphasic system to the adsorption of others, including possible ecotoxicological risks.⁵¹⁾

Some (in fact, rather many) of these substances are emitted exclusively by man—be it on purpose, as with pesticides or tensides (washing detergents) or by accident (*products* from crude oil). Many more substances are released both by nature and anthropogenically (including NO_x , SO_2 , HCl, Hg and CdO from both fossil-fuel-combusting power plants and volcanoes), with one or the other prevailing; only recently we started to appreciate which “strange” compounds are produced particularly by aquatic animals, including, for example, halocarbons, isocyanides, “mustard oils” (R-NCS) and even (bromo-hydroxy)dioxines. Substances from anthropogenic activities cover by-products of combustion or metallurgy (huts, smelters) as well as metabolites from man and husbandry or commercial chemicals, especially volatile solvents. Among the substances from both man and biota or geological sources are inorganic and organic gases like HCl,

50) Aqueous solubility of organics is linked to $\log k_{\text{OW}}$ by an empirical formula which essentially states solubilities in 1-octanol will not differ considerably, and adsorption of organics to soil/aquatic sediment rather behaves according to $\log k_{\text{OW}}$, also. Hence aqueous solubility is directly linked and related to adsorption. A tendency in organics such as adsorption will increase

among such compounds which do not at all readily dissolve in water.

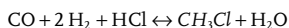
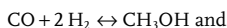
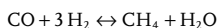
51) Organisms like the sediment-dwelling worm *Tubifex* spp. accumulate certain compounds taken from sludge. *Tubifex* in turn are eaten by fishes and water fowls (e.g., ducks), passing the contaminants back into ambient water as well as into the trophic chain up to man.

CH_3Cl ⁵²⁾ and CH_3Br , both also solids like certain metal oxides from either smelters, wildfires or erosion.

Anthropogenic inputs and natural (other than biogenic) ones differ as follows: Humans produce and use items with considerable affordances of materials and high chemical complexity or diversity: while hardly any kind of organism does need more than 25 chemical elements, a colloquial personal computer makes use of many more elements. Already when raw materials, precursors and spareparts are produced, lots of matter are moved, relocated and processed,⁵³⁾ going far deeper into soil than any plant root would be able to do, producing and partly emitting all heavy metals, salts, oxides of carbon, nitrogen and sulfur, dusts, wastewaters carrying sediments and dissolved salts plus processing chemicals—including cyanide—in much larger amounts than any other living being can afford for producing its biomass,⁵⁴⁾ most of it getting into the environment somehow and somewhere (“ecological rucksack”⁵⁵⁾). As long as the product or device is operated, it keeps (directly or indirectly, e.g., associated with production of electrical energy used by it) emitting “waste” matter into the environment, be it by consuming/ converting energy (e.g., in traffic systems, heaters), by mechanical wear or simply since the device itself produces or processes some chemicals (apart from atmospheric O_2 , fuels) besides consuming energy.

Eventually components which can no longer be used, and are hard or inconvenient to recycle, are brought to deposit pits (dumps), both official (legal) and non-official ones. There they can cause secondary emissions. Passing some stuff to the environment can even be part or scope of its use, for example, the domestic function of tensides is the dispersion and transfer of some solid or liquid pollutant to the environmental compartment water or pesticides (if used in agri- or aquaculture directly rather than in storage). Except with water-based dispersion colors, the drying of paints entails the release of solvents which—regardless of whether these paints are distributed indoors or outdoors—make their way to the atmosphere also. Landfills and other waste dumps influence the third environmental compartment,

- 52) Methyl chloride is also formed besides CH_4 in volcanoes which emit rather reducing (containing appreciable [excesses of] CO , H_2 , CH_4 , and H_2S) gas mixtures (e.g., on Kurile Islands and adjacent Kamchatka Peninsula), probably by some variety of methanation reaction in cooling gases, with ash acting as a catalyst:



- 53) Whereas plant roots or cave systems dug by animals extend to some 10 m below the surface at most, mining is done down to 4 km, crude oil and natural gas production even to >7 km below the surface.

- 54) While animals use some 5–10 times of the biomass produced, and plants give away several times the amounts of minerals to be resorbed as ligands into soil, an average citizen of an industrialized country will consume some 10 000 times his or her weight during their lifetime from fossil fuels alone.

- 55) The ecological rucksack or “footprint” (Schmidt-Bleek, 1992) gives the ratio of weights between the total mass moved in mining plus that used in processing (e.g., coke burned in a high kiln during iron production) divided by the weight of the final item produced and eventually used. For example, if 2 g of gold are extracted from 1 t of ore (a quite modest yield), the rucksack will be 500 000.

soil, both by geochemical influences and because forming an underground disposal site necessarily implies excavation which inevitably destroys evolved soil structures.

Even if liquid, solid or even radioactive residues are correctly disposed of in depositories, permanent seclusion from environmental compartments cannot be taken for granted: biological processes in anaerobic conditions can methylate semi- or heavy metals (As, Sb, Se, Hg, etc.), reduce (Hg; Wood, 1975) or carbonylate them (Ni, Mo, W), each process producing volatile products which may be vented along with disposal-site gases; leaks or underground barriers which are not at all sufficient will entail matter transfers into soil and groundwaters. Besides the above highly toxic products, landfill gases contain some 1% of benzene (i.e., comparable with car exhaust gases untreated by any exhaust gas converter!) formed by biochemical reactions involving aromatic compounds. Internal combustion engines of whatever size, including power plants and heating systems, first interact with the air by obtaining oxygen for combustion therefrom, afterwards passing "waste gases" and particulate byproducts (fly ash, dust, soot) into the air again. These solid particles are going also to be deposited on both soil and water surfaces.

Volatile compounds are going to be rapidly transported in the atmosphere; those soluble in water are moved with it in rivers, tidal streams or ocean currents. But substances which are neither really volatile nor soluble in water beyond, say, 10^{-7} g/l can become subject to fast transport too provided they get bound to (sufficiently small) particles, that is, aerosols or particles suspended in water. While persistent compounds (and element species such as noble gases, Hg vapor, or elemental sulfur) simply follow partition equilibria when spreading beyond that environmental compartment they were emitted into, reactive species behave differently, according to (usually unlike) rates of chemical alteration and partition equilibria for the secondary product(s).

For example, non-polar organic substances will stick by adsorption to likewise non-polar solid phases like humic matter, soot,⁵⁶⁾ less to polar sorbents such as silica or clays. Benzene or PAH substitution by one single hydroxygroup will increase aqueous solubility by a factor of 15–20 from benzene, naphthalene, phenanthrene and so on to the corresponding phenols, naphthols, hydroxyphenanthrenes and so on, in the same turn decreasing $\log k_{ow}$ by 2 or more, thus also changing their tendency toward the adsorption to (mainly organic) "mud". If either photo- or biochemical processes (attack by photoproducted OH radicals, activity of laccases and other enzymes) bring about the hydroxylation of non-persistent compounds, their partition among soil, air and water or among different phases or fractions of soil will change also. After reactive compounds are passed into one

56) This is the reason for the particular toxic and carcinogenic risks associated with soot from combustion: the solid, polymeric support—something in between graphite and graphene—does not pose substantial toxic problems for itself, but it perfectly

adsorbs those PAHs some of which are involved as intermediates in its very formation, including highly carcinogenic tetra- or pentacyclic ones such as chrysene, benzo(a)anthracene and benzo(a)pyrene.

environmental compartment, their secondaries—which need not at all be less hazardous to environment and biota—might pile up in any of the other two. Besides benzenoid or (smaller, volatile) PAH aromatics, this does likewise hold for aliphatic compounds such as alkenes or some inorganic species: chromates in water or soil can be reduced to Cr(III), then precipitated by, for example, phosphate, markedly reducing both their mobility and toxicity. Semivolatile but highly persistent compounds ($T_{1/2(\text{troposphere})} > 5$ years) undergo global distribution by air-flows until getting trapped by “global distillation” in cold traps like arctic or high-altitude regions, or they make their way into regions where the environment is sufficiently aggressive to enforce chemical transformations eventually, through chlorofluorohydrocarbons (CFHC) and their photolytic products in stratosphere, (allowing for photolysis at $\lambda \leq 240$ nm rather the surfacial 295 nm limit).

While the mobility of substances is very small inside soil, the production and transformation rates are high owing to the remarkable biological activities there. Geochemical pedogenesis (making soil from primary sediments or stone rubble) is also associated with pronounced transport of matter during eolian and water erosions, sedimentation and redox processes due to species which get there from either the soil–air interface or from groundwater.

The list in Table 1.3 also mentions a larger number of biogenic residues, ranging from animal and human manure, fecals over residues from cattle breeding and agriculture to oils or fats (gases like ammonia, liquids like manure and solids including entire carcasses, besides parts of plants, food- or fodder-making residues. One only gets a realistic idea what does happen here if one is aware that almost 50% of all the photosynthetic production on Earth (including oceans and arctic regions) are used or even “organized” (agriculture, forestry, cattle and fish breeding) by man for his own purposes or get caught (quite literally) without being the objective but nevertheless most likely to die in this process (“by-catches” in fish-, shrimp production, with the by-catch often corresponding to 5–10 times the “actual” prey). These 50% correspond to billions of tonnes per year, with respective challenges to extent of biological degradation of these huge flows of reduced organic matter (straw, sprouts or bones can only be partly used in agriculture again directly). Biogenic water-soluble residues pose a burden to ambient waters and (before) a challenge to technical environmental chemistry in sewage treatment plants, and so do insoluble kinds of waterborne waste (lumps of fat, large-scale organic particles, torn cellulose, plastics). Although these are removed in the first, mechanical part of a sewage treatment system already, they must be destroyed somehow thereafter, yet. Whereas combustion of biogenic residues might be attractive for releasing quite substantial amounts of energy (power plants using straw or wood fragments/saw dust/pellets or biogas), biogenic organic matter, for being biogenic, does contain all the other elements involved in biology besides C and H (and many more) which inevitably are released upon combustion, adding pollution hazards (ash, NO_x , SO_2) to the consumption of oxygen from air now (rather than of dissolved O_2 from water).

An attempt to make a mass balance is most telling: unplanned emissions outweigh purposeful inputs by orders of magnitude, with the largest ones of the

former being several bio.t/year of CO₂ and—still—large amounts of evaporating solvents, also capable of producing substantial problems due to halogen contents and an IR radiation absorption far in excess of CO₂, in addition there are N oxides (N₂O and others) and CH₄ from agriculture (degradation of excess nitrate fertilizer, rice paddies and cattle breeding, respectively) and from disposal sites (about 10⁸t/year each).

This compares to a “planned” input of some 110mio.t of NH₃ (in 2002) in ammonium salt fertilizers, some 10mio.t of tensides⁵⁷⁾ and similar amounts of pesticides (total weight of formulations rather than “pure” active agent—the latter was 2.6mio.t in 1995). The largest amount of tensides is used in oil production now, besides domestic cleaning, ammonia undergoes biological oxidation to form nitrate eventually; both the original compounds and their secondaries undergo transport and partition among the environmental compartments. Of course, tensides are going to influence this partition considerably (which is their practical purpose, after all).

1.3.3

Transport and Chemical Alteration of Environmental Chemicals

Table 1.4 shows that there are different ways of transport and transfer of chemicals in and among environmental compartments, for example, by advection (transport making use of fluid flows), diffusion, dispersion (spreading on some water surface) or transport by particles. Neither diffusion nor dispersion have certain typical ranges of speed which would allow to predict the prevalence of either transport mode or of advection in a general way, except for advection dominating over large distances. Brownian (molecular) motion occurs in random direction, causing the time to cover a certain distance to increase with the square of that distance.⁵⁸⁾

Advection refers to horizontal transport in and effected by air or water, that is, wind or water currents. While typical wind speeds are 5–7 m/s, rivers and ocean currents including tidal flows rather proceed at 1–2 m/s. Thus substances, either

57) A rough estimate which is based on the following substance-specified data on production and consumption:

- Straight linear chain alkylbenzene sulfonates which are the backbone of most anionic tensides 2.6 mio. t (in 2000);
- Fatty alcohols (long-chain primary alcohols like cetyl alcohol [*n*-hexadecanol] or polyethylene glycols 1.6 mio. t [in 2000]);
- Tensides made from crude oil/ petrochemistry constituted some 0.1% of total crude consumption in 2002 whereas about 50% of tensides were made from biogenic fats or oils

(which include classical alkali carboxylate soap).

58) In many old-style chemistry lecture halls there are vertical liquid-filled glass tubes to visualize the rate/slowness of diffusion, using solutions of colored salts (permanganates, [Cu(NH₃)₄]²⁺) which take years (≈10⁸s) to pass 1 m, with the progression of diffusion fronts going on with the square root of time which has passed by. Hence, 15 nm in a synaptic gap is covered within milliseconds at most during nerve activity. Hence in groundwater, diffusion is significant only when there is no (reason for) macroscopic flow (typically 5–10 m/year) or if very short distances are concerned (<1 cm).

Table 1.4 Processes involved in transport and removal of chemicals after they get into the environment (after Fent, 2003).

Type of process	Specific process	Chemicals concerned (examples)
Transport	Advection, diffusion, dispersion	Crude oil, atrazine
Transfer	Particulate transport	PAH
	Dissolution in water	Tensides
	Adsorption to particles, sediments and soil	Heavy metals
	Evaporation into atmosphere	Tetrachloroethylene
Transformation	Atmospheric deposition	N and S oxides, dioxins
	Abiotic (hydrolysis, photochemistry, redox reactions)	Organophosphate pesticides
	Aerobic or anaerobic biological degradation	Methylmercury cation, pesticides

dissolved or particulate, can be transported across continent-size distances within a few weeks' time.

Atmospheric flows are then directed mainly in West–East or converse directions whereas ocean currents mainly propagate South–North at the surface and counterwise in the deep ocean (e.g., Gulf, Humboldt, Benguela currents). Thus the most reactive, shortest-lived compounds which make their way to globally equal distribution although they are emitted in certain parts of the Northern hemisphere mainly, are methane and methyl chloroform ($\text{CH}_3\text{-CCl}_3$) at some five years tropospheric lifetime.⁵⁹⁾ Volatile or gaseous compounds with similar or even longer lifetimes accordingly undergo global distribution also, eventually possibly to be precipitated in “cold traps”. More reactive substances (tropospheric lifetime <6 months) like CO pass neither pass the tropopause vertically nor make it to the other hemisphere horizontally through the calm belt along the equator.

The atmospheric transport of some substances is obviously terminated by deposition, notwithstanding subsequent transport in and by water. Compounds which are readily soluble in water will be deposited by rain, fog or snow within days, limiting the ranges of transport to about 1000 km. Given the usual direction of winds in Europe, it is obvious why during the 1980s massive emissions of SO_2 from certain states or parts thereof (United Kingdom, the former German Democratic Republic, the eastern ČSSR) would hit next or second-next neighbor states

59) Lifetimes can be estimated from the reaction rates with $\text{OH}\cdot$ and (during the night) NO_3 radicals and rates/quantum yields of photodegradation by light of $\lambda \geq 295 \text{ nm}$.

mainly, separated from the emission sites by small seas at most (southern Norway and Finland, parts of Poland and Byelorussia), with this medium-range transport aggravated by “high smoke-stack policy” with stacks of up to 400 m height keeping the immediate regions clean but producing essentially laminar waste gas tracks no longer exposed to turbulent mixing which would be caused close to any rough surface in settlements or forests alike.

While transfer in water will occur in either adsorbed or dissolved forms, matters are different in air because all gases can be mixed indefinitely. Without mixing limits like among liquids or solids, the only “problem” might be the chemical (reaction) formation of aerosols (ammonium salts, Los Angeles Smog, including peroxide-induced formation of organic oligomers). However, adsorption to solid particles is very similar in either kind of fluid; such particles can be transported over continental distances if they are small enough (their density is much in excess of that of air in any case), for example, the almost proverbial Saharan dust which provides most of the Fe and Mg supply of Amazonia.

So far, these processes are merely physical ones, except for some reversible chemical reactions like protolysis with acidic or alkaline (NH_3) gases or vapors, but then transformations happen which irreversibly change the chemical identities of these substances, including both abiotic (hydrolysis, photolysis, redox reactions) and biotic processes among which latter aerobic and anaerobic ones might afford the same intermediates. The same holds and is repeated for the secondary products, which undergo transport and transfer quite like their precursors emitted originally but of course with different kinetic and physicochemical parameters. While there is no fundamental difference among the processes in environmental compartments and inside biomass, there are more possible pathways in biochemical transformations. Nevertheless there are substances which escape biochemical transformation; in addition resorption by organisms may be limited. Hence, biochemical transformations need not be the dominant ones in an environmental system, competing against hydrolysis, photolysis or redox processes. Typical kinds of biotransformations include:

- Oxidation, particularly hydroxylation;
- Hydrolysis;
- Conjugation with polar anions or organic molecules (glycine, sugars, sugar acids, etc.).

In vertebrates these are mainly accomplished in the liver and serve to enhance water solubility. As a result, they are back-extracted into the intestine (guts) to facilitate renal and/or fecal removals; for example, while simple esters such as ethyl acetate are just poorly miscible with water, all the oxidation (ethyl glycolate) and hydrolytic products (ethanol and acetic acid, respectively) are readily miscible with water. When hydroxylated compounds like alcohols or phenols are produced from alkanes, alkylbenzenes or benzenoid aromatics by peroxidases, water solubility increases once again, and finally an entire hydrophilic side chain can be introduced by conjugation.

1.3.4

Reactions and Effects

An effect is the (every) kind of influence exerted by a substance or process onto some system which changes the state of the latter. In chemical effects it is hard(-ly meaningful) to distinguish between an effector substance and processes induced by its presence: a substance gets into the system, reacts or catalyzes with some other component(s) there and produces some by-product which either causes an effect or the production of which is the very effect. This general statement holds for systems of arbitrary chemical and structural levels of complexity. With living beings being chemical systems also, biochemical effects cannot be distinguished effectively from the “purely chemical” actions of intruding chemicals.

Dissolution of polymers by acids or bases is nothing but etching injury of biological matter, while precipitation of Ca salts of certain organic acids is the reason for the development of in-organ stones or gout (if the precipitated salts accumulate within joints). Gout can likewise be caused by suppressing xanthin oxidase (a Mo-dependent enzyme) activity by, for example, diclofenac in vultures, fishes (Section 4.3.2).

Besides, biorelated chemical actions include changing solubility relationships, causing an attack on lipid bilayers in cell membranes by organic solvents, or the formation of addition compounds like gas hydrates (narcotic effects of gases including N_2 and heavy noble gases) or quinhedrones (phenol toxicity) – neither of which is considered a “genuine” chemical reaction (cf. textbooks on noble gas compounds published before 1962).

All these correspond to biological action modes: attack onto cell membranes by solvents will bring about uncontrolled – or blocked – passage of ions causing severe neurological effects, while the formation of addition compounds by nonpolar reagents causes narcosis.⁶⁰⁾ In addition there are yet more kinds and sites of action and effects: membranes give structure and divide compartments to and inside biological systems, have to be penetrated and passed by either diffusion or active transport during metabolism. Metabolism in turn spells ongoing chemical reactions which consume and produce substances on one side of a membrane anyhow; hence “simple” chemical transformations and effects from their products are superposed and modulated by reaction–diffusion coupling. In

60) The formation of gas hydrates (see also Figure 4.67) and similar addition or intercalation compounds (also in the synaptic gap, altering its width and hence lag times and acceptable excitation frequency) causes narcosis by the inhalation of narcotic agents like $CHCl_3$, diethyl ether, krypton (!) or cyclopropane (cf. gas hydrate sequestration of CO_2). If partial pressure is increased (e.g., 1.5 bar

with Ar, >3.5 bar with N_2), nitrogen, argon and so on exhibit narcotic effects also which limits their application in diving, with the high pressure nervous syndrome caused by rapidly enforced gas dissolution in tissues (by descending rapidly, say to 300 m within 10 min in a reported case) seizures, which sometimes kill directly rather than by secondary drowning.

corresponding reaction–diffusion systems there often will be chemical shaping of an environment, for example, by chemical waves (reaction wavefronts) which thus are also observed in biology, for example, Ca^{2+} ions during cell budding are obviously sensitive toward both excitation and changes in diffusion coefficient at the membrane. The membrane and its behavior can even be “manipulated” by surfacial adsorption of ions and (non-reactive, see above) gases. This brings about another mechanism for action of compounds besides “directly chemical” ones, which would entail (possibly catalytic) change of substances or solution destruction of existing structures. The threshold for such indirect effects is much smaller than with chemical interferences.

Many substances get into organisms, some of them going to be enriched, deposited over long periods of time (PCBs in fatty tissues, heavy metals in either bones or kidneys) or to undergo chemical modification, that is, partially metabolized. Some of these metabolites will cause biochemical effects of their own, for example, PAH (ep)oxidation products are epoxides (benzoxiranes) and are capable of adding to nucleic acids by opening the three-membered ring, thus becoming mutagenic and much more toxic than the original compound. Effects from this or similar transformations can be systemic or just hit certain organs of one or several species.⁶¹⁾ In quite different organisms, the effects can be very similar, for example, Pb^{2+} inhibiting Zn-dependent enzymes are involved in prophyrin biosynthesis (see above, the effect being common to animals, plants, fungi and many kinds of bacteria altogether). Likewise 4,4'-bipyridinium salts like Paraquat interfere in both animals and plants with electron transfer in the respiratory chain because the $(\text{R}_{(\text{N})2}\text{bipy})^{2+/+}$ redox potential⁶²⁾ is between those of the respiratory chain quinones, causing oxidative decoupling of phosphorylation. But they can also vastly differ by interacting with certain items (enzymes, etc.) within grossly unlike metabolic networks; examples include the high toxicities of both Cu and La toward algae (and certain moulds) but not higher green plants or that of Ag against most bac-

61) Some examples: Whereas Be^{2+} , dioxines and also 2,2'-dichlorodiethyl ether are demonstrated to be carcinogenic in the guinea pig, the latter compound now is considered not to provoke cancer in humans. In animal experiments, teratogenic effects of angiogenesis inhibitor thalidomide are small but proved catastrophic in human embryos, while action as an angiogenesis inhibitor additionally allows for its use as a cytostatic agent also (in [non-pregnant!] humans).

62) Bipyridinium salts are N-alkylated pyridines which are linked back-to-back to each other, producing a dication, that is, 4,4'-diazia analogs of biphenyls or flourenes of general formula $(\text{R}_{(\text{N})2}\text{bipy})^{2+}$. Unlike simple pyridinium salts (including vitamin B_6) which take up a pair of electrons

reversibly, but similar to C-homocyclic polycyclic aromatics (PAHs), uptake of a single electron here to yield $(\text{R}_{(\text{N})2}\text{bipy})^+$ is also possible, producing a stable free radical which is considerably stabilized with respect to PAHs as the charge of the additional electron is “compensated” by two positive charges. Accordingly the redox potential is higher, and so much higher than in PAHs (there $E_{\text{PAH}/\text{PAH}^+} \approx -1.6\text{V}$) that paraquat and its derivatives do interfere with metabolic redox reactions which take place at quinones, jeopardizing (oxidatively uncoupling) ATP synthesis. The same toxic mechanism is seen with other aromatics strongly stabilizing negative charges, like 2,4-dinitrophenolate. The reversible 1e-transfer at paraquat sometimes is used as an electron relay in photoelectrochemistry.

teria. Neither silver nor rare earth elements (other than Tb) are significantly toxic against vertebrates.

Chemical reactions and biological effects can combine to produce ecosystems effects if different organisms as well as abiotic factors get involved, causing havoc often even if growth and reproduction of certain organisms at the basis of the trophic pyramid appear to benefit (eutrophication of lakes). Effects in environmental chemistry can, moreover, cause biological damages if they change the radiative spectra reaching Earth ("ozone hole", now going to diminish): although there are some 20–40 km of vertical distance between the region of corresponding chemical reactions (HalO_x , NO_x and HO_x cycles of photoinduced catalytic ozone destruction) the UV radiation which now comes to the surface not only more but to somewhat shorter wavelengths, is capable of causing damage in all skin, eyes (cataract), and vegetation. The toxicological effects which are to be discussed now depend on direct rather than spatially remote interactions between some reagent and the metabolism of some test organism⁶³⁾ it interferes with.

1.3.5

Examples of Lipophilic Behavior, Accumulation and Toxicity: Kinds and Reasons of Effects Caused by Organotin Compounds

There is a really long history of attempts to correlate chemical structures or physicochemical parameters⁶⁴⁾ to toxicity data or other dimensions of biological activities of substances, starting much earlier than corresponding work on (substituent effects in) chemical kinetics by Hammett (1973). The theoretical precondition for deriving such data was the theory of molecular structure (entities which exist in 3-D space, joined by chemical bonds between atoms), designed in the 1860s, which additionally, besides such spatial structures, postulated some relationship between these structural motifs and chemical reactivity.

As soon as one tries to describe such relationships by numerical parameters one ends up with a description which contains some kind of quantitative structure–activity relationship (QSAR) statements, the oldest corresponding approach dating back to this very time (Crum Brown and Fraser, 1868). Although comparative studies (comparative among chemical elements, not different animals or plants) date back at least to 1825 (Gmelin, on dogs), the periodic system of elements

63) Test organism here does not necessarily correspond to the whole-organism test, toxicological laboratory experiments or even active biomonitoring (see also Chapter 4.1.1.2, Definitions) but it simply denotes that effects are studied on a certain, given species or cell lines derived from it.

64) Typical quantitative structure–activity relationship (QSAR) descriptors include substituent constants which refer to changes of reactivity (in kinetic terms) by introducing some peripheral functional

group to a standard reactant system, for example, an arene (Hammett, 1973; Exner, 1972) or an alkene (Taft) while topological indices are focused with spatial arrangement of atoms in a molecule (including Hückel and HMO (Hückel molecular orbital) MO theories), or correlations which implicitly deal with HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital) energies, for example, by using redox potentials or spectroscopic properties.

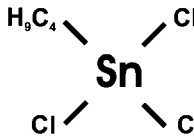
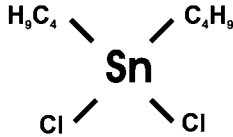
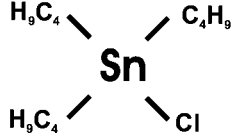
inorganic tin Sn LD 50: ?	MBT = monobutyltin  LD 50: 2140 mg/kg BW
LD 50: 1360 mg/kgBW  DBT = dibutyltin	LD 50: 70 mg/kgBW  TBT = tributyltin

Figure 1.7 A comparison of toxicity data for inorganic and butylated tin compounds in rat (Oehlmann and Markert, 1997). BW: body weight.

(Mendeleyev and Meyer, in 1869) was required for any systematic treatment. Some time later the term “heavy metals”, now considered by many to be meaningless in toxicological terms, was introduced in 1904 for this very purpose. Soon after, the redox series of chemical elements was linked to their toxicity, an idea which was recently revived by Lewis *et al.* (1999). There are very sound and illustrative treatises on QSAR approaches which make use of either “purely” empirically chemical data or terms from quantum chemistry, topology and the like (see Schüürmann and Marsmann, 1991; Schüürmann and Segner, 1994; or so far as PAHs are concerned, see Balasubramian, 1994; Borosky, 1999).

In species which are centered on tetravalent tin, if the chloroligands are replaced one by one by *n*-butyl groups, the lipophilicity and log k_{ow} will obviously increase considerably, accompanied by a tremendous increase in neurotoxicity and the propensity to accumulate⁶⁵⁾ along the trophic chain (Figure 1.7). Certain marine mollusks (snails) experience hormone-analogous androgen activities of R_3Sn^+ (tri-alkyl tin cation) ions, causing genital malformations (Oehlmann *et al.*, 1996). By

65) In certain cases, reaction between cobalamine (aquaform of vitamin B12) cobalt centers and alkylated metal or semi-metal compounds are reversible,

stripping alkyl groups from the latter rather than just producing biomethylation by methylcobalamine, but this does not occur with tin.

some QSAR approach, the effects of this stepwise replacement of Cl by $n\text{-C}_4\text{H}_9$, which concern the reactivity toward certain functional groups—including hormone receptors in organisms—can be taken in quantitative (QSAR!) terms. Moreover, while $\text{Sn}^{\text{IV}}\text{-Cl}$ bonds undergo ready hydrolysis (SnCl_4 is a volatile liquid “fuming” with HCl cleavage in moist air—*spiritus fumans Libavii*, after its sixteenth-century discoverer Andreas Libavius), Sn-C bonds are much more stable, but attacking sulfur centers to become irreversibly bound to proteins.⁶⁶⁾ In 2004, the use of tributyltin paint additives for ships [hitherto used to preclude the attachment of algae and the larvae of sessile animals (mussels, barnacles, corals, sponges) on vessels, which increased their water drag] was banned for ships of >25 m total length. Besides this, triorganotin compounds were used in organic chemistry ($\text{Bu}_3\text{Sn-H}$ as H atom radical source, e.g., to start polymerization) and even, in the direct vicinity of human skins and bodies, for the disinfectant treatment of textiles!

1.3.6

The Term “Heavy Metals”⁶⁷⁾ and Its (Purported) Chemical and Toxicological Ramifications

Whereas covariances between the (metal/elemental) density and the toxicity of chemical elements were noted as early as 1904, the relationship thus suggested was recently dismissed as a “non-descript term” (Nieboer and Richardson, 1980) even though it became really popular even in commonplace use of language. Since cation formation can cause substantial changes in atomic/ionic radii, solid-state properties of elements are unlikely to be related directly to chemistry. However, toxicity was observed to increase (often) with the oxidizing properties of a metal ion, like with Ag^+ , Hg^{2+} , Tl^{3+} , Au^{3+} or Pd^{2+} , or among the different oxidation states of vanadium, but the far less oxidizing uranyl dications are also highly (chemo-) toxic. So there should be a relationship with electron affinities in both atomic and ionic states which partly is due to the relativistic contraction of orbitals. This both increases electron affinity, and thus redox potentials, and reduces atomic radii, producing higher elemental densities of sometimes $>20\text{ g/cm}^3$. In addition, affinity to sulfur binding sites (Shaw, 1961), including the capability to cleave disulfide bridges in proteins by oxidative insertion (Hg_2^{2+} , Au^+ , Pt^{2+}), has a role in this “heavy-metal effect”. Toxicological correlations between oxidation potential and, for example, its (oral) toxicity toward *Rattus norvegicus* (Lewis *et al.*, 1999) does imply some assumption on biochemistry in the target organs, namely what will happen to the oxidation state and binding form (speciation) of an element in the body. If one cannot define the oxidation state and binding form (speciation) of an element in the body, no oxidation state of a given xenobiotic can be identified (notwithstanding problems of redox and complexation kinetics) and there is no

66) Polyalkyl tin or -lead ions are poor acceptors in coordination chemistry, producing feeble bonds to halides, oxospecies or thiolates, whereas neutral ligands hardly attach at all.

67) For the definition of the term “heavy metal” please have a look on footnote 35.

way to define any redox potential; thus, the above correlation then cannot be established at all.

Though not really arbitrary, oxidation potentials have but limited validity in bioinorganic chemistry as the actual array and concentration of active ligands in biomass is poorly known (even though a parameter for average coordination behavior of biomass samples can be deduced from biofractionation properties; Fränzle, 2010), putting some doubt on toxicological conclusions linked to the above oxidation potentials. However, as noted before, the attack of certain heavy metal ions in lower oxidation states [in fact, all the heaviest non-radioactive elements of all ($Z = 75\text{--}83$) except for Tl and Bi, which are too hard to oxidize to react with perchalkogene moieties] is typical, observed with those metals almost in general and with many organometal compounds: cleavage of disulfides by oxidative insertion which affords thiolatocomplexes of Hg(II), Au(III), Pt(IV) and so on. As these disulfide linkages are ubiquitous in biochemistry except perhaps for some organisms dwelling in extremely reducing environments, such as clostridia or methanogenes, these elements are strongly toxic regardless of taxa or even kingdoms of life; the respective heavy metals are likely to inhibit most of those transformations which are accomplished in environmental engineering making use of organisms. Sewage treatment plants may succumb if there are too much heavy metal in inflow water, and the final limit of phytoremediation is heavy-metal toxicity. There are some plants which tolerate substantial levels (e.g., ferns like *Diopteris vittata* or various *Thlaspi* weeds) but they are very small, their roots only capable of cleaning the uppermost few centimeters, and their growth is slow; hence, phytoremediation is surfacial in either sense of this word and going to take a very long time. Nowadays relativistic numeric quantum chemistry is advanced to such a level (Pyykkö, 2000) that this insertion process (Sperling and Steinberg, 1974) and other typical features of elements with $Z > 70$ are accessible to theoretical treatment, besides experimental work.

Given this, why should there be any relationship between metal density and toxicological features of its chemical properties? Empirically, all metals of $Z < 23$ are light metals ($\rho \leq 6\text{ g/cm}^3$) and in addition display class A behavior as defined by Ahrland, Chatt, and Davies (1958). For $Z > 50$, all but Eu are heavy metals in the above definition, moreover, class B behavior is quite general except for REEs (Nieboer and Richardson, 1980). The reason is as follows (Fränzle and Fränzle, 2002):

Atomic radii do not significantly increase from Li or Be (the lightest metals at $Z = 3$ and 4, respectively) up to the said $Z \approx 80$ heavy elements owing to relativistic orbital contraction (the binding energies, and thus mass gains, of the innermost electrons then are about 20% of their rest masses, making these orbitals shrink by >15%); hence densities should increase almost like atomic masses by 20–30 times, and they actually do so [cf. Li ($\rho \approx 0.53\text{ g/cm}^3$) and Pb (11.3), or even $Z = 74\text{--}79$ ($\rho = 19\text{--}22.6\text{ g/cm}^3$)]. Now, at $Z > 70$ there are lots of electrons rather closely packed which thus strongly interact regardless of their allocation to correspondingly many orbitals (spin–orbit coupling also is a result of special relativity). This large number of similar orbitals at higher fundamental quantum

numbers permits electrons to escape correlation to some extent, making use of another orbital very similar or even identical in energy. Accordingly, polarization readily occurs in both metal and ionic states, and the ions become “soft” (class B) to prefer the binding of donors like iodide, phosphines or selenium compounds. With both mass and charge of atomic nuclei being large, the attraction of the outermost electrons becomes strong. Hence, for $Z > 74$ these are fairly hardly oxidizable (except of Tl), often even noble metals, while their ions can be readily deformed and thus polarized and hence they readily bind to heavy chalcogens or pnictogens (S, Se, As, etc.).

1.4

How to Determine Environmental Pollution

1.4.1

From Methods of Trace Analysis up to Understanding the Underlying Processes

Analytical data “as such” do just provide information on concentration levels and distributions of elements and compounds which are measured. If we deal with trophic chains or networks, distributions among food and certain organs of the body or the relationship between soil and (given part of higher) plant concentrations, the values so obtained are obviously linked to each other. This may correspond—or serve to check the latter—with ideas on which processes are involved in transport between the pairs of compartments or element matrices which are considered. Such processes include diffusion, with or without the formation of complexes, in active transport in organisms, which is accomplished using and consuming ATP, and “leaching” of soil solids by organic acids which behave as ligands and are delivered into the rhizosphere of both trees and grasses. Models which account for these transport processes necessarily draw upon “chemical” concepts and terms for description purposes. Now we must turn to the purposes of environmental sciences and also applications in environmental engineering which are the factors and biogeochemical features to control and direct the fluxes of both elements and compounds through some trophic chain or—spatially—across an ecotone, regardless whether this transport is “wanted” (biofortification, bioremediation) or rather causes problems and hazards. Obviously, this is related to running plants like sewage treatment plants.

Because chemical compounds can bear a number of different functional groups which are themselves comparable to those of the more abundant chemical elements and in addition can almost freely combine⁶⁸⁾ most of these functional groups—two or more different of them—in a single molecule, their chances to undergo quite diverse chemical reactions (some of which will spell cleavage of pollutants) are far larger than those of inorganic ions, including oxoanions of both

68) Except for spatially close pairs of functional groups which interact inside or among (a) molecule(s) to yield either polymers (polyamides including peptides, polyesters) or salts (including cyclic sulfonium or ammonium [aziridinium] salts) readily.

non-metals (Si, N,P, As, heavy halogens) and metals like V, Cr, Mo and so on. Thus a detection and quantification of elements by trace analysis, coupled to a determination of environmental parameters pertinent to chemical potentials (pH, Eh) allows for a rough estimate of toxicological conditions only, and the same holds for the range of biochemical transformations (including biomethylation) then possible, whereas the stabilities of functional groups like aldehyde or nitro moieties may also be limited. For very nonpolar compounds or metabolites, bioaccumulation can occur (which is very rare in inorganic species), increasing biological effects regardless of whether these compounds remain in their original states and adhere to lipophilic receptor sites much as, for example, steroids would do or cause narcotic behavior or become transformed into other compounds or ions which then can react with corresponding receptors and other biochemical items, sometimes even irreversibly. While toxicity values do not differ vastly among the speciation forms of most metals, matters are quite different concerning non-metals such as F, Cl, P, N, or As. Here pH and Eh really matter. If there is nonbiological enrichment owing to low volatility and/or strong adsorption (which also tends to increase with $\log k_{ow}$), these processes will amplify the effects of increased toxicities of certain speciation forms and bioaccumulation to cause grave adverse effects even though only a minute part of the said element (non-metal or Sn) is present or converted into such a form. Examples include dioxins formed both during forest wildfires and in waste incinerators, the photochemical formation of the former by UV excitation of PCBs and the halogenated phenylphenols formed thereof. Besides strongly increased toxicity, adverse properties might persist over generations:

- Not only dioxins but also otherwise harmless compounds like solvent dimethyl formamide (DMF) can be strongly teratogenic, causing congenital but not genetic malformations in embryos or fetuses, while in addition:
- The number and structural manifold of mutagenic agents⁶⁹⁾ is far larger among organics than in heavy-metal salts, with the effects of mutagenic agents persisting over many generations.

Both features co-act to further increase both the extent and the spatiotemporal range of implications and effects due to such compounds. Fortunately, this fatal cooperation is somewhat alleviated by organic substances being (usually) more readily degradable—and degradable in other, more diverse ways—than inorganic ones; however, they tend to accumulate in trophic chains. This increases the concentrations of ultratrace pollutants to such an extent that endocrine disruptor effects on polar bears in the Arctic (Svalbard Island; Wiig *et al.*, 1998) and alligators in the south eastern United States (Guillette *et al.*, 2000) become obvious, as was the decline of large birds feeding on fishes, other birds or carcasses of dead

69) This statement mainly refers to humans and their kinds of exposition. Both other mammals, including rabbits to which Be salts or TCDD are acknowledged to be carcinogenic and newts which possess

these fantastic abilities to re-grow lost limbs completely but are the more sensitive to chemical perturbations which can have these repairment mechanisms run readily out of control.

mammals (see below). In former decades, the principal agent to blame for this was DDT, the endocrine properties of which influenced Ca uptake into eggshells so much that the eggs still laid down could no longer be bred without destroying (squeezing) them, after DDT ($\log k_{ow} = 6.8$; Verschueren, 1983) had accumulated in the fat of fishes eaten by, for example, ospreys or white-bald eagles. These endocrine effects tend to hit top-level consumers only, but even second-level consumers can suffer in certain situations also: like in humans, *Diclofenac* [3,5-dichloroanilinophenyl-2-acetic acid,⁷⁰ as the Na or $\text{NH}_2(\text{CH}_3)_2^+$ salt] was until recently commonly used in veterinary medicine as an analgesic and anti-inflammation agent. However, there was a real collapse in vulture populations in India and Pakistan which ate the carcasses of beef or goats treated like that. As a result, carcasses lie around much longer than elsewhere in these hot climates, spelling increased risk of epidemics. In any case, such an almost complete removal of top-level consumers—be it by excessive hunting or chemical impacts which hurt reproduction—is going to cause grave effects on an ecosystems all the way down to producers.

The processes and effects of organics (not just phenols which directly resemble estrogens in structure motifs) are thus going to hit—though indirectly—more and more different species in some ecosystem than “inorganic pollutants” (would) do, owing to the propensity for bioaccumulation. If the latter occurs to such an extent that toxic, reproduction-toxic or other endocrine effects become considerable next to the top of local trophic chains, the derivation (in fact, devouring) from biomass, components thereof and the population dynamics are influenced in all the lower trophic levels also. Ecological stoichiometry studies did underline the effects of consumer-driven nutrient recycling (Vanni *et al.*, 2002; Elser and Urabe, 1999) that the (effective, average) length of trophic chains also is relevant for the distribution of bioaccumulating organic pollutants in the biota: once top-level consumer populations are destroyed in an ecosystem, the average lifespans of the lower-level consumers (or even plants) tend to increase which means that they will accumulate higher average levels of the said organic compounds. The problem also exists with inorganic toxic elements such as Cd, but at least these do not undergo biomagnifications via consumers. Heavy metals might cause problems though even if they are essential (excess Cu, Mn, V, or even Fe being considerably toxic) but the effect is not amplified via the trophic chain as these elements are not going to biomagnify—except perhaps for some which readily undergo biomethylation to form products stable enough to be handed up the trophic chain (As, Sb, Hg, possibly Bi and Pb^{71}).

70) While just a few species of vultures are vulnerable to this effect, which brings about kidney failure and muscular inactivation, none of them are new world vultures (of which condors are more closely related to storks rather than old world vultures). 3,5-Dichloroanilinophenyl-2-acetic acid also readily passes through sewage treatment systems without any

degradation and just limited adsorption. However, it can readily be degraded by sensitized photochemistry (Fränze *et al.*, 2010; Chapter 4.3.2).

71) For the neutral methyls (as far as is known, other alkyls or aryls are formed only with As and Hg) $\log k_{ow} < 5$. Accordingly, biomagnification is feasible only.

To put it into a nutshell, it is essential to supplement trace element analysis by speciation analysis to get any idea, let alone prediction on processes and consequences linked to the presence of certain elements in apparently unusual concentrations. Speciation analysis is already required to understand the processes as such, to find out whether precipitation, biomethylation and adsorption to particulate organic matter or to sediments occur at all. These processes of course are controlled by solubility and the well-known effect of $\log k_{ow}$ on adsorption also.

Even then, demonstration of causal relationships remains an issue, because correlations among certain factors can never give proof of the ideas on models or on causality at all, regardless of how large the correlation coefficients or levels of significance may become. Popper's venerable principle that the falsification of a working hypothesis must be (i) both possible at all and (ii) feasible in an operational manner cannot be readily applied to macrosystems in environmental sciences. These macrosystems which often are investigated in environmental sciences possess highly sophisticated feedback structures which can bring about non-linear or even oscillatory behavior and their dynamic complexity cannot be grasped simply, making it very difficult to test hypotheses on their modes of action in a convincing manner. But moreover, there are severe ethical concerns in doing corresponding experiments, given that many of the effects on both structures and functions of ecosystems would be irreversible. Then reasonable concerns that problems arise from ongoing anthropogenic changes should urge us to correct mis-developments before the full-scale damage has been done and becomes irreversible. Examples of such anticipation of severe problems and corresponding measures already mentioned in this volume include the greenhouse effect and the other CFC-related issue, ozone destruction.

Nevertheless it must be maintained that hypotheses concerning causes, effects and modes of effects in environmental sciences must be formulated according to the same strict criteria as elsewhere in the exact sciences, that is, both conform to the laws of nature, including the principle of causality and being liable to experimental (or observatory⁷²⁾ falsification. Later Nobel laureates Svante Arrhenius,⁷³⁾

72) It is not just a drawback of environmental sciences that: (i) certain clarifying experiments cannot (ought not) be done for ethical reasons (the same with medicine!!) and (ii) observation and numerical simulation of natural processes must replace an actual experiment (cf. astronomy: stars are not directly accessible, let alone subject to experimental manipulations, and even testing thermonuclear warheads would not correspond to or be suited to simulate any phase of evolution of a star . . .). Accordingly, environmental sciences cannot be dismissed as "soft" sciences as long as Popperian criteria are fulfilled by acting like in other areas of science

(medicine, astronomy) to gain evidence in the sense of empirically robust knowledge hard and unlikely to falsify any time later.

73) Note that his seminal work on the greenhouse effect (1896) had no relationship to those branches of physical chemistry the development of which would Arrhenius earn a Nobel seven years later: this was on the formation of ions in conventional chemical systems, simply by the dissolution of salts or acids or bases, and these ions being the reason for electrical conduction and the feasibility of electrochemistry in such (aqueous, alcoholic, etc.) media rather than in salt melts only.

Sherwood Rowland and Mario Molina (to name but a few) were motivated by such thinking to issue stern warnings based on chemical and spectroscopic reasoning much before that level of evidence on the corresponding topics could be gained which shapes contemporary discussions and measures.

1.4.1.1 Inorganic and Organic Compounds

Environmental sanitation cannot and should not be started unless one has a sound idea of the situation around. For this purpose, concentrations of chemical compounds, all “autochthonous”, biogenic and anthropogenic/xenobiotic, must be determined by some analytical procedures and, given that toxicities (especially of non-metal compounds) sensitively depend on the mode of binding, this must be done in a couple of different ways. There are more general ways (technical methods) of analysis which are restricted to the presence of elements only, disregarding (or destroying during sample preparation, if there is any⁷⁴) any information on chemical bonds these elements are/were integrated in. As chemical elements are generally considered to be “inorganic” items (a relic term from the times of vitalist views disregarding that biotic and non-biogenic samples, molecules, etc. in fact consist of the same set of chemical elements), the elementary analysis is called inorganic analysis. Moreover, the detection and determination methods in inorganic analysis usually depend on atomic or even nuclear [instrumental neutron activation analysis (INAA), mass spectroscopy, Mössbauer spectroscopy] properties while organic analysis (and speciation, see below) deals with and makes use of the properties of complete molecules or molecular ions (even though these molecules are not always unchanged after the analysis).

There are some kinds of analysis which can be done on the raw sample (just dried) but which do not afford information on binding modes or oxidation states, except for Mössbauer spectroscopy. These are called direct methods (direct because chemical sample preparation is avoided) and include neutron activation analysis (INAA), X-ray fluorescence spectroscopy (XFS, based on Moseley’s law), laser-pulse induced mass spectroscopy (MALDI-TOF) where some surface sample is evaporated and ionized by intense optical radiation, some varieties of graphite-furnace atomic absorption spectroscopy and the chemical information obtained by XFS when this kind of emission is excited by an electron beam during scanning electron microscopy.

So “inorganic” and “organic” analyses actually draw upon (and sample) different levels of matter organization hierarchy. Since valence electron binding energies are smaller than those of the innermost K shell (1s orbital) electrons or that among nucleons by many orders of magnitude, doing chemistry (if unwanted) is far easier

74) It is noteworthy that both the latter and MALDI-TOF can deal with effective sample sizes smaller than 1 μm , that is, in a range of <1 pg actual sample weight, allowing just a few thousand atoms of trace components to be detected. In crystals, XFS also provides some chemical information by the shift of onset

frequencies which is also obtained in Mössbauer spectroscopy but is there limited to a few elements and rather high concentration levels. MALDI-TOF might still provide certain chemical information if ions thus formed are not degraded to atomic ions but retain most or all of their chemical bonds.

to accomplish than nuclear transformations (even if the latter avoid electric repulsion when using neutrons⁷⁵). Organic analysis calls for more gentle methods of sample preparation and separation (extraction, chromatography) than inorganic analysis where often chemical binding patterns are deliberately destroyed to obtain some kind of sample (digested, dissolved, liquid, open to injection into some spectrometer) which is almost standardized with respect to the remaining components (e.g., an aqueous solution of nitrates or oxometallates of most different elements). In organic analysis, the molecules (including polyatomic ions from acetate or the like up to large anions) must be conserved while separating them first from their (usually biological, as there are few organics in minerals other than kerogen, lignite) matrix and then during separation of a organic analyte mixture. The former is usually accomplished by extracting the sample with some organic solvent(s) while the latter is done by some variety of chromatography, most commonly gas or liquid chromatography. After this step, the molecules may well be destroyed during identification unless the ultimate purpose is preparative natural product chemistry rather than analysis. This, for example, occurs in GC/MS where the molecules separated during gas chromatography are not retrieved but sent to a mass spectrometer which inevitably destroys them. Matters are different with high-pressure liquid chromatography (HPLC) where methods of identification leave molecules as they are (absorption spectroscopy or fluorescence spectroscopy).

Instrumental analysis:

1) *Inorganic compounds*

This is focussed on elements, destroying their original organic matrix to obtain solutions of element cations then to be analyzed without regards (which then are no longer available) to speciation forms.

2) *Organic compounds*

This deals with entire molecules (both neutral and charged) extracted from a matrix as they are. Here, speciation is an issue provided the combinations of chromatographic separation and identification allow one to grasp all the (major) speciation forms of the element. The identification is more critical than separation, especially if standards are lacking. This is fairly common in the diverse mixtures of compounds found both in biomass and in multiple- or diversely polluted sediments at sites, for example, carbochemistry includes the processing and application of coal tars. Nuclear magnetic resonance (NMR) and mass spectroscopy may be helpful in actually identifying the components of such mixtures.

75) This is also the message told by the history of sciences: whereas deliberate chemical reactions date back far before scripture was invented, the first nuclear transformation was accomplished only in 1919 by Rutherford [^{14}N (α , n) ^{17}O] and

radionuclides (unstable nuclei) were prepared only during the 1930s [first, ^{27}Al (α , n) ^{30}P] simply because much higher energies are required to start nuclear reactions [controlled (thermo-)nuclear fusion still is a challenge].

1.4.1.2 Speciation and Concentration

Except for the noble gases and alkali metal ions heavier than lithium, all chemical elements on Earth exist in gaseous or liquid phases in a larger or smaller number of different binding forms (i.e., notwithstanding their inclusion in most different solid phases like salts and minerals or primary forms created by radioactive decay in any environmental compartment or water). These so-called speciation forms include volatile or non-volatile halides, oxides, complexes of metals and often organic compounds many of which latter are produced by living organisms. What matters here is that often these different binding forms—speciation forms—vastly differ from each other and from the plain chemical element involved in terms of toxicity and also bioavailability. To understand and appreciate whether a given environmental concentration of, say, fluorine, arsenic or chromium actually poses a toxicological and thus environmental risk, one has to know about its kind of speciation or distribution among various speciation forms. Often already changes in ambient redox potentials will alter the situation gravely, perhaps more often for the worse than for the better, unless specific strategies are applied. Anyway, speciation must be determined and the array of methods applicable for this purpose is called speciation analysis.

Speciation covers various binding forms of the same element (except for elements existing in but one kind in the environment, e.g., cesium as aquated Cs^+ ion besides being part of certain minerals) and there commonly are several contributions of unlike compounds or ions to a total concentration in both the environmental compartments water (including raindrops), soil and in biomass. Concentration thus means a total concentration which is the sum of all these contributions, while there are individual concentrations for each of the species forms. Owing to different lipophilicity ($\log k_{ow}$, e.g., after biomethylation or complexation to compounds like phenols), volatility and propensity to form ions (sometimes also due to biomethylation, e.g., with As, Se, Sn^{76} , Hg) and hardly soluble salts, these speciation forms almost always display strongly differing distributions among the environmental compartments and biomass. In addition, their stabilities toward oxidants like O_2 , OH and NO_3 radicals also vary widely. For example, selenium can be readily volatilized from wet, reducing soils as dimethyl selenide but, once in the air, it will be attacked by OH radicals within minutes, and hence its average concentrations in air remain very small. While a total concentration can readily be determined after oxidizing digestion, speciation analysis brings about high challenges to separation techniques: (i) in organic analysis or ion chromatography to identify inorganic and simple organic ions, where the charges on the species to be separated will match or at least have the same sign, (ii) in speciation analysis we are often concerned with a mixture of all neutral, anionic and cationic entities of vastly different lipophilicity, polarity, solution behavior and so on. Hence, as a rule, it is not possible to get hold of all the speciation forms using a single kind of chromatography. There is an exception for heavy non-metals

76) While inorganic tin tends to hydrolyze into SnO_2 (cassiterite) rapidly, biomethylation is usually incomplete, producing organotin cations of different positive charges.

and some metals (Sn, organo-Pb, Bi, Hg) which can be volatilized by hydride reduction to afford volatile (alkyl- or aryl)hydridespecies.

The (concentration) terms ‰, ppm, ppb, ppt and ppq refer to different levels of dilution (10^{-3} , 10^{-6} , 10^{-9} , 10^{-12} and 10^{-15}), respectively. This may be depicted in transferring the problem to two dimensions (spatial areas): a stamp has an area of some 7 cm^2 . With the stamp lying somewhere on a colloquial desk ($\approx 1\text{ m}^2$), it covers about ‰. If it lies down in your city house backyard garden (some 500 m^2), it will cover something like 1 ppm of the garden's surface. This same stamp in a small village site is equivalent to about 1 ppb. In a large city (some 700 km^2), like Hamburg or Birmingham, it corresponds to 1 ppt of surface area. Eventually, for the United Kingdom or Texas, it amounts to about 3 ppq of area. Figure 1.8 gives a visual example of the terms ‰, ‰, ppm, ppb and ppt after Markert (1996).

1.4.1.3 Quality Control of Analysis

In addition to the similar need for highest representative quality of the sample to be analyzed, most general rules and prerequisites of quality control in chemical analysis have to be taken into account (Markert, 1996; Markert *et al.*, 2003a,b). In the past 20 years a strict differentiation between the terms “precision” (reproducibility) and “accuracy” (the “true” value) has been established in chemical analytical research (Figure 1.20, Section 1.6.3). The practical application of this differentiation makes it possible to determine the “true” or real content of substance “X” in sample “Y”. The purpose of determining the precision of the data by repeatedly measuring the analytical signal is to track down and eliminate errors which might be generated, for example, by insufficient long-term stability of the measuring device (device-specific misadjustment). If the analytical procedures are not too complex, the precision will be 1–5%, and for most analytical problems this can be considered sufficiently exact. However, the mere fact that a signal is readily reproducible does not permit any statement about its accuracy. Even highly precise data can diverge greatly from the “true” (e.g., element) content of a sample. Correct analytical results can only be obtained if the entire analytical process is subjected to targeted quality control, where every result is checked for its precision and accuracy. Basically, two methods are now used to check the accuracy of analytical results: (i) use of standard reference materials (commercially available samples with a certified content of the compound to be measured and a matrix similar to the original samples to be measured in the laboratory) and (ii) use of independent analytical procedures.

A more difficult problem is that of accuracy during the sampling procedure, for at present we have no “certified reference system” as a calibrator for accuracy in representative sampling. As a rule, “polluted” and “unpolluted” systems will be compared, but there is no way to be sure of working accurately. The only possible strategy here is that of “independent methods”, when different research groups have the task of working in the same area with the same indicators, so that the data—obtained independently—can be compared. This is a very expensive method that can only be used in very special cases where method development is of general

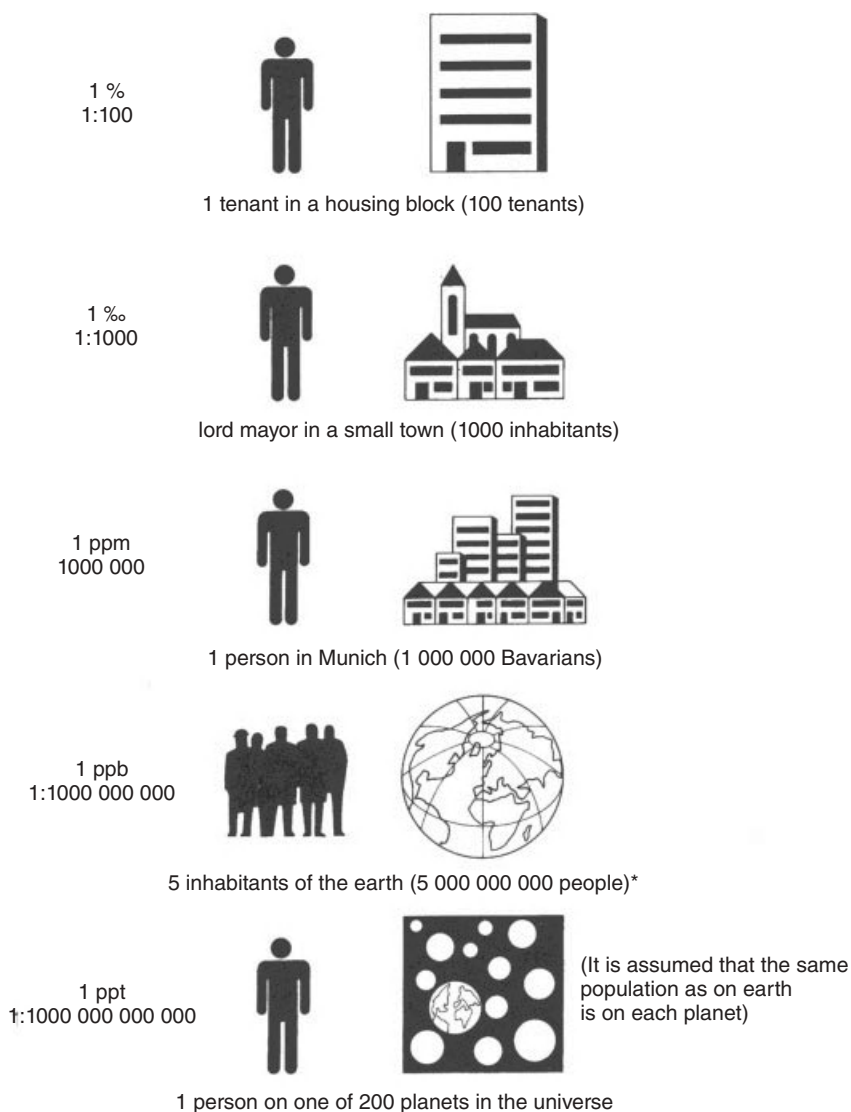


Figure 1.8 Illustration of the terms %, ‰, ppm, ppb and ppt. In extreme trace analysis the measuring range is often even lower by a factor of 10^3 , that is, in the ppq range (e.g., in the case of samples with a relatively low level

of dioxin and platinum metal pollution; Markert, 1996). *For sure, at the moment (2011) more than 7 000 000 000 people exist on earth.

concern, for example, for directives issued by the European Union (EU) or the United States.

1.4.1.4 Accreditation of Laboratories⁷⁷⁾

Accreditation now is an issue in many areas of society and its infrastructures. Certification by institutions within the EU is key to constructing, for example, the European Common Market. Certification is a means of politics of harmonization which aims at EU-wide legal harmonization by using guidelines to make legal norms as identical as possible. For this purpose, criteria of identical structures of laws and norms are supplemented by implementing and demanding identical procedures of certification. In doing so, European certification politics go beyond harmonization, because they also cover those areas which are voluntary and not covered by common legal norms (Berghaus, 1994). An end of European politics concerning certification and accreditation is to facilitate mutual acknowledgment of tests and certificates in order to avoid costly multiple tests of the same subject. This takes measures which create mutual confidence by the utmost degree of transparency (Berghaus, 1994).

Concerning universities, accreditation of studies apparently is an instrument of reliably maintaining and increasing the “quality performance” of certain studies, by means of an accreditation procedure which is done on a regular timescale and itself checked within reasonable periods of time.

However an example from analytical chemistry shows that undergoing a process of accreditation does not by itself provide some better or more accurate result. Figure 1.9 shows the outcome of a telling international experiment run by Paul de Bievre’s workgroup (with the EU-run “Institute for Reference Materials and Measurements” in Geel, Belgium).

This investigation was a round-robin analysis which belonged to IMEP-6, the International Measurement Evaluation Program “Trace elements in water”. The organizers sent identical samples of water (natural river water, the composition of which they knew exactly; Clear Creek, Colo., USA) to a total of 165 laboratories in 29 different States, asking them to determine 14 trace elements like lead (Pb) or cadmium (Cd). Groups of laboratories all over the world have taken part in such round-robin analyses for many years now, providing valuable information on the performance of certain analytical laboratories with respect to both accuracy and reproducibility of measured parameters. In addition, IMEP-6 generated information on accreditation, simply by asking the involved laboratories to state whether they had undergone accreditation, certification or other procedures designating them “officially acknowledged in analytical chemistry” (“AAA”-ranking) or not before taking part in IMEP-6.

Figure 1.9 shows the result for Pb level measurements in the water samples by either “non-accredited” (a) or “accredited” (b) laboratories: just a few among the non-accredited laboratories obtained the certified value of $0.133 \pm 0.003 \mu\text{mol/l Pb}^{2+}$ (value $\pm$ confidence interval) but the “accredited” laboratories did not perform

77) According to Markert and Konschak (2003).

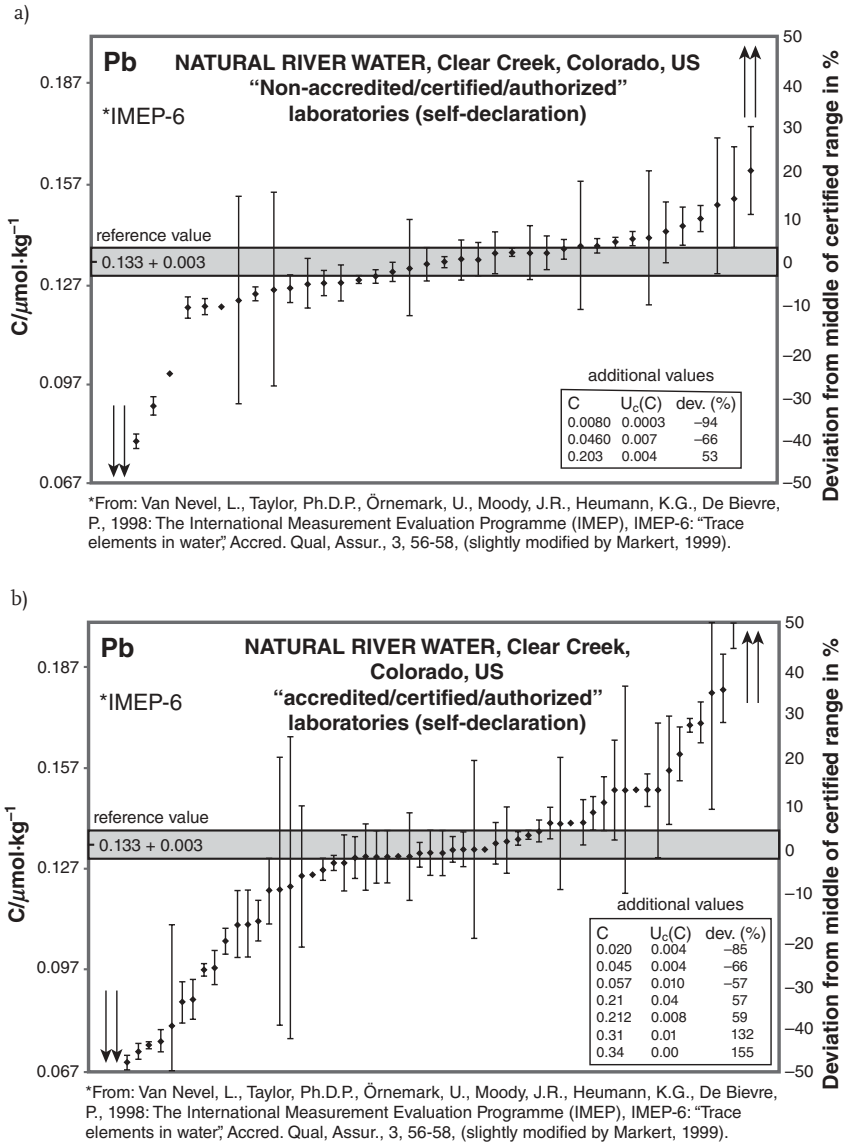


Figure 1.9 A comparison between quantitative measurements of Pb in "natural river water" (Clear Creek, Colo., USA) among "non-accredited" (a) and "accredited" (b) laboratories which took part in IMEP-6 comparative analysis (modified from Van Nevel *et al.*, 1998).

better (Figure 1.9b). The general result of IMEP-6 was that accreditation did not (positively) discern accredited versus non-accredited laboratories with respect to quality of results obtained by them, or, to put it frankly: "... there is little correlation between the self-assessment of the laboratories and reality..." (Van Nevel *et al.*, 1998). At least for this investigation prior accreditation of

laboratories did not improve accuracy of measured data and thus the quality of measurements.

1.4.2

Physical Methods in Chemical and Environmental Analysis, Modeling Ecosystems and the Role of Ecotoxicology in Integrative Environmental Sciences

Ever since people started to try to understand biological processes in quantitative terms of mass transport, transformation and accumulation, that is, like looking at chemical reactions, they obviously chose and employed chemical methods of analysis and “book keeping.” Probably the first to do this was Dutch chemist Jan van Helmont early in the seventeenth century. He noticed that a small seedling would be able to become a tree of 100 kg total weight or more within several years, taking water and the components of wood ash from the soil while carbon was apparently obtained from air somehow during photosynthesis. Around 1840, Liebig made use of elementary chemical analysis⁷⁸⁾ of plant biomass to translate these data on inorganic biochemistry (which had not yet been given this name) of biota into strategies to improve and sustain agricultural productivity. Liebig’s key results were the principle of minimum in theoretical and mineral fertilizer application in practical, applied terms. Much later, this body of knowledge was transferred from systems concocted by man to spontaneously arranging ecosystems, assaying nutrient cycles, generalized element cycles and limitation to ecosystems net productivity along that way of reasoning. Sometimes, corresponding experiments were done in open biocoenoses on an appreciable scale, for example, when trying to control and enhance CO₂ uptake by algae in the open ocean (Aumont and Bopp, 2006), fertilizing scores of square kilometers by Fe(II) additions. Given the scarcity of iron in the ocean, the idea was to increase photosynthetic productivity and have the algae escape C recycling by their sinking to sea bottom and becoming a (rather inactive) part of the sediment, but it turned out that most of them were eaten still in the photic zone, thus jeopardizing carbon sequestration.

Of course, similar experimental work was also done in systems which have a well-defined outer edge and limitation, like a couple of inter-connected small lakes in Canada. Besides measuring the pathways of various elements through these lakes and the local biota, the latter biota was arbitrarily changed in composition, length of trophic chains and so on by introducing novel consumers or else removing (catching, fishing almost) all of the creatures which represented certain trophic levels. It turned out that such complete removal of top-level consumers⁷⁹⁾ might seriously alter the aquatic chemistry of lakes and also seriously influence the ratios

78) Looking at the history of element discoveries, you will notice that this was about the earliest time such an approach could be done, given the fact that the most reactive of the major elements present in a plant than had just recently been identified and isolated. This holds for both essential

(K, Mg, Mn), sometimes essential (Si, Br) and non-essential (Al) elements likewise.

79) Keep in mind that these need not even be part of the in-lake biota but can also be adjacently living air-breathing vertebrates preying on fish or zooplankton, like bears, otters, ospreys or even flamingoes.

among species of lower trophic levels. Therefore, corresponding experiments are an ethical issue now also, but their role in the history of empirical ecology (and ecological stoichiometry) went far beyond learning with regard to the effects of unwanted or, to say the least, uncontrolled N or P inputs as the sense of the problems got sharper. This sense of the problems in turn did not just change their accepted and preferred choice of methods in experimental ecology but also had an impact on the expectations that society [in the USA, Canada and most parts of (western) Europe] would direct to the implications and importance of these—primarily chemical—kinds of works in environmental research.

1.4.2.1 Analytical Chemistry

“Purely” experimental manipulations in aquarium tanks, mesocosms like lysimeters or small ecosystems (like the above lakes) were augmented and partly replaced by investigations of ecosystems in their actual states, be they close to natural, significantly perturbed/polluted or even recently originating from anthropogenic activities, like lakes forming in quarries or open-mining pits or highly unstable man-made association of organisms in agricultural systems. During the past 50 years or so, sensitivities of analytical gear increased tremendously, with solid-state microelectronics allowing much work to be done on site rather than making all the analyses in the laboratory after removal of the samples and (all too often long-distance) transport. Thus many species, both inorganic and organic, could be determined down to the levels which are ubiquitous in the environment (for many trace elements, like rare earth elements, the actual levels in living organisms such as terrestrial green plants are still lower—nothing like bioaccumulation here!). During the twentieth century, several, now most important instruments, were developed for analytical purposes, like mass spectrometers (Aston, 1922), column chromatographs (Tswett, 1906) and, later, gas chromatographs (for historical beginnings and developments, see Martin, 1952), electrochemical analytical procedures, neutron activation analysis or X ray fluorescence spectroscopy.

These methods could then, additionally, be linked to each other, the results thus referred to as *hyphenated* methods, including most diverse ways of detecting organic compounds or metal ions after prior separation by some kind of chromatography. For example, it is most commonplace to attach a mass spectrometer to a gas chromatograph (GC/MS; Figure 1.10) for obtaining additional pieces of information which then allow (sometimes, at least) the identification of volatiles.

With analytical chemistry thus benefiting from technical progress and outright innovations, one now could ongoingly grasp the complexity of environmental processes and transformations (and the sizes and kinds of human interferences within those) in its “real” dimensions. Systems sciences added methods to deal with this complexity which had long been felt rather than seen by way of numerical simulation. Although electronic calculators (computers) were very helpful in this development, eventually allowing the running of ever more sophisticated models of in-system interactions on any PC available in laboratory or office, the mere fascination of “number-crunching” for purposes of outcome simulation (“change the start parameters a little bit once more and see what happens then”) often



Figure 1.10 Some kinds of analytical commonplace in technical environmental chemistry. Left: A mass spectrometer in which the required atomic cations are produced in an electrically heated plasma torch (ICP/MS) which thus is meant to determine elemental



contents. Right: A gas chromatograph fitted with a mass spectrometer (GC/MS) designed to detect and quantify volatile (mostly but not necessarily organic) compounds (photos by Stefan Fränzle).

tended and still tends to obscure reasoning in systems sciences to address causal relationships. Phenomenological reproduction of observed behavior is not the same as actually understanding it, but understanding is required in order to change the chain of events in those cases where pollution has to be tackled. However, numeric reproduction should not be considered a wrong approach either, since often there are no solutions for modeling equations whatsoever in terms of differential equations and thus one must resort to numerical simulation. The same holds if non-steady processes are to be described, say in combustion analysis inside engines which is mainly non-steady, including ignition and the explosion of gas/fuel/air mixtures, to be studied by spectroscopy (“glass-cylinder engines”; Winkelhofer and Fraidl, 1998) or—partly—by numerical simulation. The same holds that there is no alternative to numerical simulation for non-steady processes. Starting with a paper by Robert May from 1976, chaos theory got most popular even outside the scientific community although its beginnings are far older [Laplace around 1800 for celestial mechanics (Laplace, 1902), Poincare around 1900, Lorenz (1963) for the limitations of weather forecasting].

1.4.2.2 Geographical Information Systems

Geographical information systems (GIS) maps permit one to superpose different sets of space-related data in a manner which gives additional information on mutual dependences among different phenomena. Of course, ecological problems such as net productivity depending on either climate or the availability of certain nutrients can be tackled in this very manner, also. An early example of GIS applied

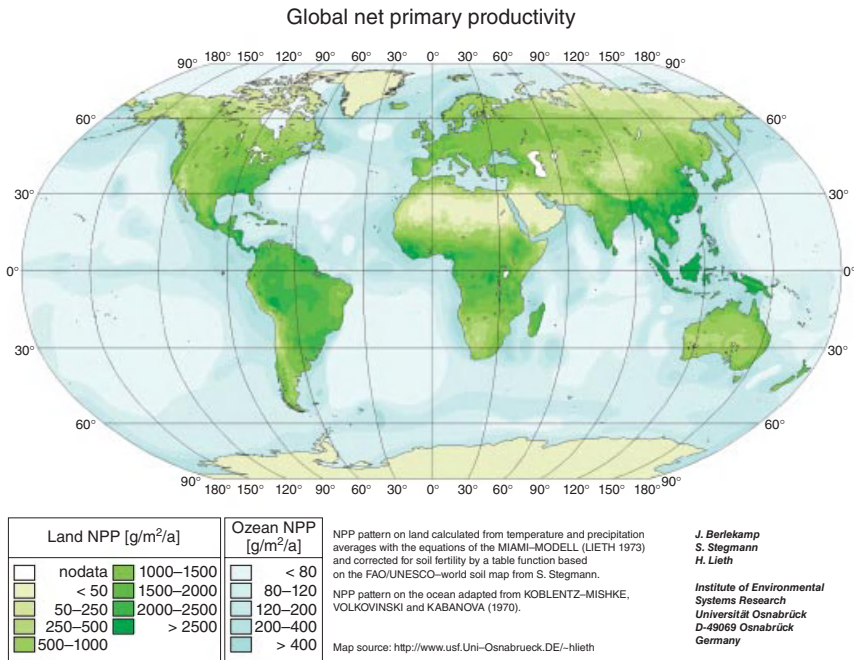


Figure 1.11 Rio Model 1995 (corrected for effects of soil fertility) for global net primary (photosynthetic) productivities. GIS/Arc Info Map, courtesy: Helmut Lieth, <http://www.usf.uni-osnabrueck.de/~hlieth>.

to global ecology was the net photosynthetic productivity maps by Lieth (1995, Figure 1.11). Here quite diverse (possible) effect causes, like climate (average temperature, solar photon flux rates), water availability (e.g., Sahara desert and tropical rainforests⁸⁰) on about the same geographical latitude) and certain nutrients in the ocean. This is relevant in everyday work rather than just to historians of science as these particular GIS maps contain some message on the chances to bind CO₂ by vegetation purposely grown in certain regions and thus also states of the world. This is significant given the Kyoto Protocol allows for validating—and trading—CO₂ cleavage activities linked to re-forestation of certain areas promoted or funded by others to “buy” emission certificates. Moreover some highly industrialized countries which are in an economic position to buy emission rights are not only densely populated but also distinguished by very low net photosynthetic productivities, including their marine surroundings if the countries are insulas or peninsulas. Examples include Korea (either part), the United Kingdom and the

80) As there is almost perfect nutrient recycling (plus some inputs by Saharan dust across the Atlantic Ocean), the Amazonian hylea is best suited to mislead people on its net productivity, which is

close to zero, rather like in the Sahara or Gobi deserts. You will soon notice this when you try to extract nutrients on a regular scale by doing agriculture there without recycling in the *terra preta* mode.

western parts of North America. Accordingly, these areas are going to be net producers of CO₂. Even though the situation is considerably better for the rest of Europe (outside UK), a mere 7–12% of carbon dioxide produced there can be reclaimed by its “own” vegetation at all.

GIS maps are also very useful, for example, in moss-monitoring campaigns (Figure 4.7, Section 4.1.15).

1.4.2.3 Biotest – Biological and Ecotoxicological Implications

With physicochemical parameters such as pH, concentrations of certain (other) compounds and UV luminosity being measured in some environmental compartment, the actual biological and ecotoxicological implications and a description of the drawbacks of chemical changes for living beings or entire ecosystems can only (at best) be inferred in an indirect way. This takes an extrapolation from what is known about optimal or marginal (respectively) living and reproduction conditions in terms of chemical effects thereon of certain species to the ecosystems metalevel. Of course, results thus obtained may be more or less clear or ambiguous; for example, the discussion on the reasons for forest dieback and the possible causal chains involved went on for more than 20 years. The reasoning which prompts and makes one design some biotests is quite different. One can, so to say, turn this approach upside down: some (a group of, for statistical reasons) test organism(s) can be brought to a polluted environmental site or brought into contact with some sample taken therefrom (e.g., exposing fishes, snails or zooplankton crustaceans like *Daphnia magna* to sediment samples⁸¹⁾) in order to evaluate physiological changes caused by this exposure, usually done over a defined period of time (say, 48 h or 30 days). Among the range of corresponding effects are:

- Rate (percentage) of test organisms to die within the given period of exposure time;
- Reproductive toxicity, including all budding rates of bacteria, sterility of metazoans, egg dieoff, embryo or hatchling deformations, miscarriage rates and deformations of genitalia caused by endocrinic activities of some compounds;
- In animals, changes of behavior [reaction time lags, aggression, speed of swimming, coordination in tricky environments (e.g., when balancing on some pole), changes of preferring dark or bright surroundings, reduced capability to cope with labyrinths or other difficult to grasp environments, etc.];
- Changes of skin color (bleaching, pathological pigmentation, short-term effects in animals which – like many fishes and cephalopods – use skin color or

81) This setup allows for testing limnetic (large river) sediments with marine organisms among which certain snails are most sensitive toward tributyl-tin endocrinic effects, or vice versa, exposing suitable freshwater organisms to seaside harbor sludges for evaluating the

toxicological properties of the latter. Likewise terrestrial sediments or mineral/ore/mining residue samples can be contacted with either freshwater- or seawater-dwelling test organisms (e.g., Matthiessen and Gibbs (1998), Leung *et al.* [2004]).

pigment pattern changes as signals), damages inflicted on certain surface organs (leaf interface, skin), including tumorogenesis;

- Production of “marker” compounds for chemical stress, including induction of enzymes and protecting agents like metallothionein or ethoxyresorufin-O-deethylase (EROD), an enzyme from fish liver cells which is induced by the addition of pollutants like dioxins.

EROD induction has a peculiar advantage for the detection of chemical stress, being hardly suppressed itself by the action of xenobiotic compounds (Whyte *et al.*, 2000). Accordingly, EROD test sensitivity surpasses that of most toxicological standard test procedures.

Figure 1.12 gives an example for outlining a biotest which makes use of permanent swimming inhibition of water fleas (*Daphnia* spp.) with their being dead being taken as the measured criterion (first item in the above list). Notably, it is still obscure what is the causal relationship—biochemical, neurophysiological or other—between the damaging effect measured in the biotest and the kind of purported environmental burden. For example, an enzyme may be inhibited or else misactivated by some heavy metal ion⁸²⁾ or a carcinogenic agent. In addition, the less related the test organism and the measured parameter are to the manner in which the human metabolism works, then the transfer to humans (or a third taxonomic species) must be demonstrated much more stringently. The conditions in which test organisms can or must be kept will dictate some selection from the above list and a hierarchy of the possible effects of intoxication which might be observed (from minor changes of behavior to death, hatchling deformations or sterility). Rational reasons must be given for which effect is to be selected (see Schüürmann and Markert, 1998; Oehlmann and Markert, 1999).

Let us consider an example of most clever biomonitoring. Among the numerous weakly electrical fishes, mormyrids like *Mormyrops kannume* (elephant fish, called so for its mouth forming a kind of proboscis) produce electric signals which are small (peaking at a few volts at most) but repeat very frequently and stably as long as the fishes feel well. In polluted waters, both the frequency of repetition and the shape of a single pulse will alter. In some drinking water supply plants this was and still is used to control water quality levels. The particularly attractive feature of this biomonitoring approach is that such electrical signals are most suited to automated digital analysis, much better than, for example, changes of color, behavior,⁸³⁾ or reaction times. Mormyrids hardly, if at all (only certain species) reproduce

82) As noted elsewhere in this volume, replacing Zn by Co in zinc-“dependants” often renders them *more* active than before. However, Co²⁺ is considerably toxic while the required daily intake of a human is a few micrograms(!), just about 5% of this being vitamin B₁₂. Accordingly, the increased activity of “cobaltified” Zn enzymes will get coupled enzyme reaction out of their mutual balance of turnovers among coupled biochemical pathways;

hence some intermediates will pile up or get depleted.

83) Yet, average swimming speeds and changes thereof caused by the impact of chemicals (corresponding to both “panic”, trying to avoid the substance, and to partial inactivation) can be monitored by determining the position which aquatic animals maintain in a conical (rather than cylindrical) flow tube.

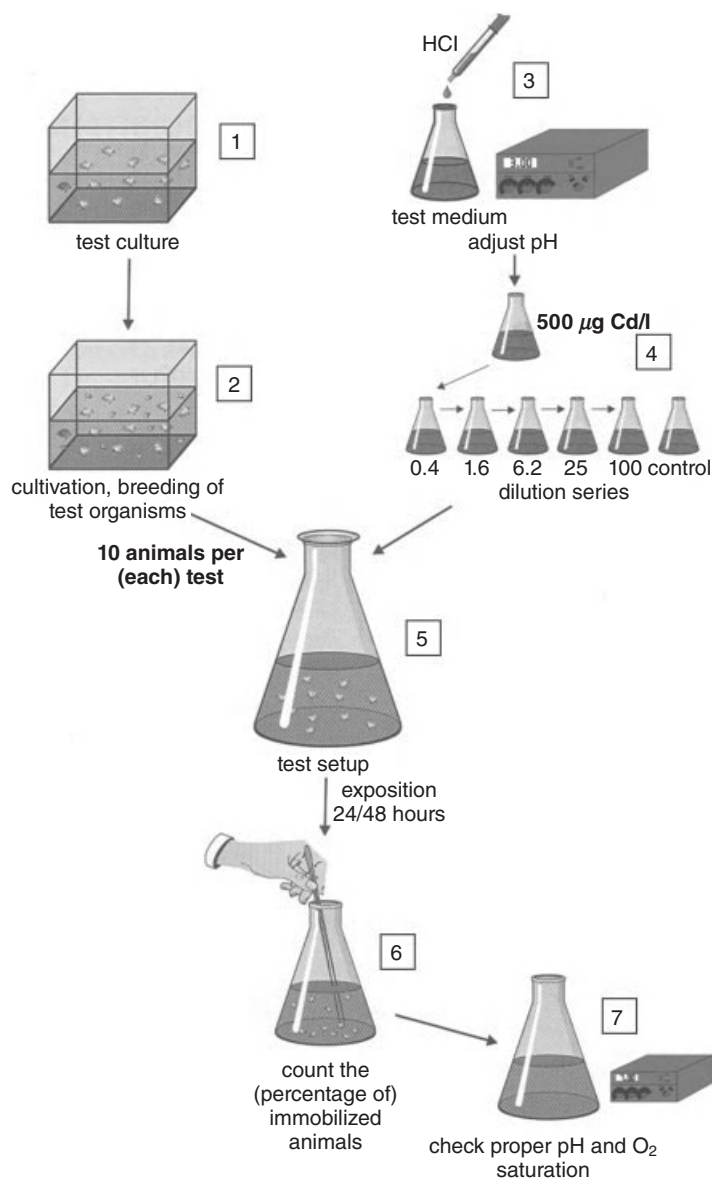


Figure 1.12 Schedule of tests on acute toxicity using *Daphnia magna* (see Fomin, Oehlmann, and Markert, 2003)). (1) Test culture, (2) breed the test organisms, (3) reducing pH of test medium to 2.5 to 3.0, (4) make a dilution series of Cd^{2+} salts: 0.4/1.6/6.2/25/100 µg Cd/l (four replicates

each), check pH again, (5) add test solution (10 young *Daphnia* per test setting), (6) count and remove those *daphnia* which became immobile (after 24 and 48 h), finally (7) check pH and oxygen content after termination of test.

in aquarium captivity, and hence studies based on reproduction toxicity are excluded [unlike with, e.g., fellow fishes *Poecilia reticulata* (guppy) and *Danio rerio* (zebra fish)]. While aquarium rearing must accordingly be considered somewhat stressful to mormyrids, the method of analyzing electric signals is considered reliable. Parameters other than reproduction toxicity which can be detected with mormyrids in aquaria of course include death and neurophysiological changes, the latter being better addressed by their intrinsic electrical activity than by changes of behavior. It must be pointed out however that, as these electrical signals are also involved in intraspecific communication, including mating behavior, fishes must be kept single for water quality surveillance to avoid perturbations by this kind of communication among the fishes (there are both solitary and swarm-forming species among mormyrids and their relatives). This is a telling example of the complexities involved in using animals, especially social animals, in biotests. Yet, among the >500 species so far employed in biotests (Markert *et al.*, 2003a,b), many are social animals with corresponding intraspecific communication avoiding perturbations of behavioral patterns, like rats or magpies (*Pica pica*).

Notably, there is no statement whatsoever associated to the effects used in biomonitoring as to the origins (causes) of the observed effects. It may be most difficult to identify the reasons of what is happening to plants, animals or bacteria under supervision. Notwithstanding this, a biotest still provides a “directly biological” statement on the possible effects of chemicals put into the environment. Accordingly, biotest and chemical analyses are a kind of complementary approaches to gain pieces of information on the “state of the environment”. In biomonitoring, being a quantitative approach, both are linked by using organisms to get information otherwise to be obtained from chemical analysis. Of course, scaling must be understood for the given system (Fränzle, 2010): you must know already how much lead is to be expected in leaves or fruits of some plant (species or cultivar XY) once a threshold level Z is surpassed in the underlying soil.

1.4.2.4 Locating Soil Pollution Sites by Geoelectric and Other Means

In both air and water environmental compartments, the principal components are fluid and mobile, causing a possible pollutant to be removed and distributed (usually rapidly) far around, starting from a given site of emission. Thus it can be detected far around by either analytical gear or biological effects after a short while. In soil, however, mobility is low, concealing pollutants often to the next vicinity of their origins, whereas heterogeneity of the soil system in chemical terms is thus conserved along all three dimensions. As, soil, moreover, is impossible to penetrate by light, precluding both photochemical alteration of components and optical spectroscopy, the detection (and remediation) of soil-borne pollutants must rely on something other than electromagnetic radiation next to visible wavelengths. For example, different kinds of pollutants may change certain soil properties in rather different ways. In turn, soil is highly variable with respect to its electrical and magnetic properties [consider inclusions such as Fe_3O_4 (magnetite) in B horizon iron pans or deeper layers], with biological attack on—especially

organic–soil pollutants in anaerobic conditions often vastly changing the corresponding parameters:

- When iron (Fe)-reducing bacteria (FRM) consume organics (and they will do so with quite a number of substrates, including mineral oil and benzenoid aromatics), the ambient paramagnetic Fe(III) is converted into the ferromagnetic materials maghemite $\text{Fe}_2\text{O}_3\cdot\delta$ and eventually magnetite (Lovley *et al.*, 1987), producing local magnetic aberrations which can be detected from above the ground.
- Direct input of salts or acids will increase groundwater electric conductivity, and both might also originate from the onset of (now, aerobic or at least hydrolytic–there are plentiful exo- or postcellular hydrolytic enzymes in common soils) the degradation of halocarbons, esters and the like, besides direct input by spills.

As an example from archeology, earlier activity at a site can of course be pinpointed by finding [stone, metal (tools, weapons, coins), ceramic or wood] artifacts but likewise by alterations of the soil chemistry. Phosphate ions pile up there from either toilet sites or the remains of dead bodies in graves (even in the case of urn graves, as phosphates do not change during the incineration of a dead body; Zöhlitz 1980a,b). Likewise there are other chemical signals persisting long after oil spills, digging away various poisonous wastes and so on. Besides affecting or even killing soil organisms, some of which actively try to escape such chemical challenges,⁸⁴⁾ the physicochemical features of soil will change also: salt spills increase electric conductivity, as does acid attack on clay minerals,⁸⁵⁾ and new interfaces in the soil created by chemical changes or an altered ground water level can be detected by seismic means (sound waves).

Soil bacteria and other organisms can “translate” chemical impacts into either magnetic signals–by producing partly reduced and thus ferromagnetic Fe oxides–or they can bring about changes of conductivity: producing organic acids will increase electrical conductivity, as will sulfide oxidation in mine tailing areas to yield sulfuric acid which is so good an electrolyte that it has now been used as

84) For example, earthworms. There is a test in ecotoxicology which just draws upon this behavior: in an octagonal basin separated into eight sections which have been filled with soil and “inoculated” with earthworms, one or several chambers are then treated by some chemical which possibly irritates or intoxicates the earthworms. If so, and if they do not die almost immediately (i.e., the applied dose simply was too large), they start creeping over the barriers into adjacent, untreated soil compartments to escape the nuisance. When doing so, they must come to the surface and can be observed directly or

surveyed by video camera. Escape behavior to evade chemical toxicity thus can even be put into comparative, semi-quantitative terms.

85) Whereas clays are pretty good electrical isolators even when rather wet, acidification below pH 4.2 will make them break apart chemically, leaving behind solid, still isolated SiO_2 (amorphous silica to sand) and rather mobile Al^{3+} and alkali cations which produce substantial conductivity moving around in ground water. Of course, the protons and acid anions (mainly NO_3^- and SO_4^{2-}) will also contribute to electrical conduction.

such in electrochemistry for more than 150 years continuously. In either case, perturbations which alter the speciation of elements (Fe, or S, respectively) by different redox potentials—pointing to admission of either organic reductants or of O₂ via cracks or in landfills and so on—cause readily detectable changes in the electric or magnetic or electromagnetic (georadar-based inductive signals) of soil, thus permitting one to look into it without digging or drilling for samples. Of course the methods are “blind” (insensitive) to pollutions which neither cause such changes chemically or biochemically or directly change conductivity (as buried metal scrap, in the most extreme case, would do). Isolating layers like clay do not pose very significant obstacles, however.

In addition, some animals use methods closely related to geoelectrics for both communication (area definition, mating) and spotting their prey which, in an aquatic environment, will differ from surrounding water, underneath sediment and so on, also by grossly different electrical conductivity. When at all active, potential prey will disclose its position by nerve and muscle electrical signals even when buried/hidden in the sediment. These electrical signals (peak voltage $\approx$ 150 mV) are passively registered and used by, for example, hammerhead sharks, freshwater dolphins and platypuses; these animals will likewise reliably find a small battery dug into the sediment unless it is empty. Electric fishes such as mormyrids rather use active ranging, relying on their own emission of electrical impulses, like man does in remote sensing. These are weakly electric fishes incapable of using electric hits for attack or defense directly (3–5 V peak voltage at most).

So, like with the former example of iron (Fe)-reducing bacteria (FRM), the bacteria which use Fe³⁺ to oxidize organic nutrients, including petrochemical compounds, which include benzene, toluene, ethyl benzene and xylene(s) (BTEX) aromatic hydrocarbons (Lovley, 1991), subterranean metabolism will alter the physical properties of (either wet or dry) soil in a manner accessible to remote sensing. In addition, this process of iron reduction also influences retention and distribution of many other elements (Crowe *et al.*, 2006), for example, stopping the adsorption of As(V) to Fe oxide phases. Hence it becomes both feasible and urgent to detect pollution sites covered by soil without drilling literally millions of boreholes throughout the landscape—which no one could afford, let alone the risk of opening potential hazard sites which were hitherto contrived. So let us first consider geoelectric and geomagnetic methods of detecting differences between polluted sites and their surroundings. In fact, besides environmental surveillance these methods are also—and about as frequently—used to pinpoint other traces of former human activities, namely, in archeology.

The maximum in conductivity (minimum electrical resistance) which marks the very spot/region where a body was buried is due to the salts the body contained. After decomposition of the body, these salts in body liquids remained at the spot, increasing conductivity. The minima on either side are due to brick walls limiting the tomb, much like a sarcophagus (Matias *et al.*, 2006).

While this is small-scale, and thus appropriate for cases where the location of a soil pollution (e.g., an old landfill or spill site) is fairly well-known and just requires to get an idea of spatial limitations, the following example shows how large the

scale of such investigations can become: it is possible to “look” into soil, sediment and rock rubble some 100 m deep while areas of dozens of hectares or even some km² can be screened. Here the task was to look for anomalous conductivity in a valley on a Greek island (Kefallonia) some 4.0 km long and 1.5 km wide which now rises some 180 m above the level of Ionian sea, which limits it both north- and southwards, linking a peninsula (Paliki) to most of Kefallonia somewhat east of here. The idea to be tested was that this valley was created only fairly recently by some landslide closing an isthmus between East Kefallonia and what (if true) had been an island of its own before (contributing another hypothesis to the ongoing controversy where to locate ancient “Ithaca”—not necessarily the island thus named today—as mentioned by Homer). If so, deep layers should be a “chaos” of intruding, highly conductive seawater and well-isolating large boulders one of which can still be seen hanging over a famous beach site and display high but heterogeneous electric conductivity. Notably, conductivity measurements were done by airborne electromagnetic (inductive) methods rather than boring poles into the site and apply voltage to them, much like magnetic anomalies like iron ore stockpiles are detected.

So investigations are feasible from decimeter to kilometer dimensions, looking deep into the ground. Even larger depths ($\gg 100$ m) and scales can be tackled by seismic rather than electrical, electromagnetic (“georadar”) or magnetic methods.

1.5

Biological System of the Elements

The Biological System of the Elements (BSE) was designed originally (some 20 years ago) by Prof. Bernd Markert (Markert 1994a) to connect pieces of (analytical) knowledge concerning a set of different plant species most of which live near to each other in and around some bog in Lower Saxony (Markert, 1996) to features of biochemistry and bioinorganic chemistry. The principal approach was to compare abundances of elements (both metals and non-metals, >40 in total) among a larger number of plant species, producing pair-wise abundance correlations over the entire set of plants (Figure 1.13), by plotting for example, the analytically detected amounts of Al versus the corresponding Ca concentrations in the same set of (13) plant species (and all the other pairs).

Thus to produce an empirical relationship between abundances:

$[M]_{\text{species}}$ and $[M']_{\text{species}}$ of the kind:

$$[M]_{\text{species}} = k*[M']_{\text{species}} + c$$

Sometimes k can be very small, for example, when comparing abundances of rare metals like V to those of very abundant (but not necessarily essential) ones such as Al, and usually there is considerable scatter in the data (i.e., $r^2 \leq 0.15$), for example, for comparisons among (most) rare earth elements (Ce vs Pr, etc.), except Y. In extreme cases the above equation becomes almost meaningless ($r^2 \approx 0$, the

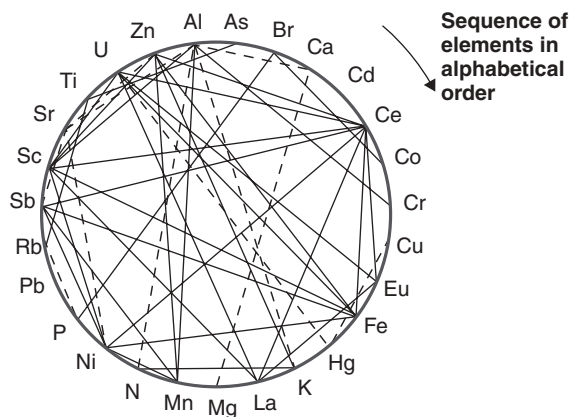


Figure 1.13 Element pairs that are either highly positively correlated (solid line) or highly negatively correlated (broken line). From Markert (1988).

concentration–value pairs being randomly scattered rather than forming some line, that is, across the set of plant species, the abundances $[M]_{\text{species}}$ and $[M']_{\text{species}}$ are not at all related), and in fact originally (Markert, 1994a, 1996) the focus rested with the correlation coefficients rather than the above original equations. These coefficients are given in the subsequent figure (Figure 1.14) which, notably, is just a cross-section through the entire space of correlations (>1000 in total number).

As a rule, Ca, Mg, Fe and Zn are the most abundant metals in plants, plus substantial though “useless” Al, lots of Cu in arthropods and mollusks both of which use Cu complexes (haemocyanine) for oxygen transport in respiration, and much Mn in green plants. In animals, compositions of major metals are similar, when considering soft tissues only, thus omitting the large amounts of Ca and the like in bones from analytical consideration.

But what is the chemical meaning of all this, and how is it related to chemical properties of elements which determine: (i) their chances/rates of uptake by roots/animals guts (from all food, water, sediment) and (ii) of retention, with usually a substantial extent of organotropy? When looking upon the majority of non-radioactive elements (+ Th, U), pairs of elements as defined above will combine all pairs of essential elements (say, an abundance correlation Mg/Zn, some 100 correlation pairs in total assuming some 15 essential elements, including the principal non-metals, except O), of one essential and one non-essential element (Al/Fe; Ba/Ca; some 200 pairs in total). Of course, also pairs of non-essential elements (like different rare earth elements; the large majority of entries) and, eventually, pairs which contain elements which are essential only for some of the investigated plant species (e.g., Si vs anything). The problem of abundance correlations may likewise be related to uptake pathways which sometimes are identical for two elements (Mo/B; S and As or Cr in strongly oxidizing, aerated conditions). Anyway, there is nothing like “biological groups of elements” akin to the periods of the chemical PSE: chemically similar or closely related elements may (different

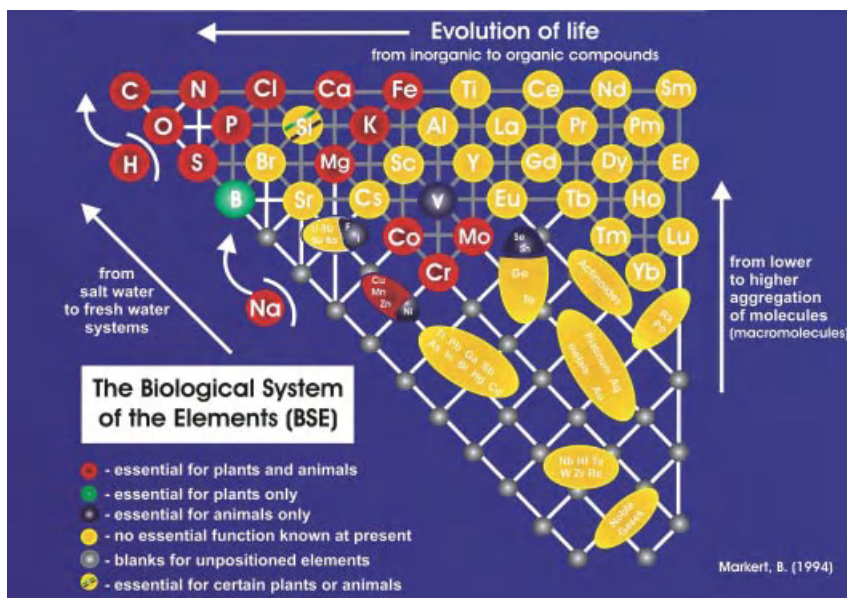


Figure 1.14 The Biological System of the Elements (BSE) compiled from data on correlation analysis, physiological function of the individual elements in the living organisms, evolutive development out of the inorganic environment and with respect to their uptake form by the plant organism as a neutral molecule or charged ion. The

elements H and Na exercise various functions in the biological system so that they are not conclusively fixed. The ringed elements can at present only be summarized as groups of elements with a similar physiological function since there is a lack of correlation data or else these data are too imprecise (Markert, 1994a).

rare earth elements, $\neq$ Eu) or may not (P/As; Ca/Ba) get fractionated pairwise from the background in different kinds (species) of plants. Three features are quite important:

- 1) Chemical coupling in one principal (large turnover) metabolic pathway involving biocatalysts which do contain (and use) different elements;
- 2) Ecological stoichiometry;
- 3) Responses to some change in metabolic conditions.

Moreover, it must be asked to what extent are the responses due to external element composition, that is, fractionation, related to environmental conditions, or are fixed by genetics? The phenomenon of ecological stoichiometry suggests the latter to prevail, as do more deep analyses of biomass–metal ion interactions,⁸⁶⁾

86) The more thorough formal analysis by Fränze (2010) proved for certain examples (e.g., birch trees; data taken by Markert, 1996) that the propensity of biomass samples (here, certain plant organs like

leaves) to retain some metals, comparing it to selective binding features of small-molecule ligands, remains untouched by whether these plants were grown on “good soil” or in highly polluted environs or even

while biomonitoring would not be feasible if this kind of biochemical control of chemical compositions would operate perfectly in variable environments. One reason for the latter is that there is no general way of removing excess inputs of elements, that is, excretion is less well defined with respect to uptake. Now, for the above three features:

- 1) *Chemical coupling*: oxygenic photosynthesis requires a balance between photoinduced activities of Mg- (chlorophyll, CO₂ binding protein rubisco) and of Mn-containing (photosystem II) biomolecules. Structures of all three molecules being almost universal,⁸⁷⁾ efficient water splitting and electron transfer (from water oxygen) to sequestered CO₂ will take some constant stoichiometric relationship of both photosystems: one (Mg-based) subsystem must reduce CO₂—bound to ribulose-bisphosphate originally—at the same rate (x molecules per leaf cell and second) as the other (Mn-based PS II) oxidizes water, save for some stoichiometric factor (which indeed is very close to one). Otherwise some substantial part of the electrons thus moved “uphill” will be “wasted” into either making elemental hydrogen (which nevertheless may happen in isolated chloroplasts) or CO₂ is absorbed and chemically bound without soon being reduced, making intermediates pile up with severe expenditures (“wasting”) of ATP. Because of the large dimension of this turnover in any photosynthetic organism, the larger share of both Mg and Mn are employed in this activity. One can predict the above Mg/Mn ratio in photosynthetic organs of green plants—regardless of its being leaves or needles—to be rather constant.
- 2) *Ecological stoichiometry*: in a more general reasoning, living organisms are found to exhibit some chemical composition which—within one species and concerning the most abundant biorelevant non-metals C, N, and P only for now—is about as constant as it would be in a daltonide⁸⁸⁾ molecule. Say, C:N:P = 3:1:1 in serine phosphate and $x:y:z$ in some (part of an) organism

on pure sewage sludge. Hence the chemical composition which provides the binding sites for metal ions (11 different kinds of possible ligands in the side-chains of the 22 proteinogenic amino acids alone) and controls the tendency for retention and sometimes accumulation of metals is actually given by genetics, with considerable differences observed in closely related (e.g., different *Vaccinium*) species (data taken by Markert, 1996).

- 87) Rubisco (almost entirely identical protein sequences) is likewise used by autotrophic bacteria and cyanobacteria to fix CO₂, and photosystem II also is genetically highly conserved even though the structure of high oxidation state mono- or

oligomanganese dioxo systems is not at all critical for their giving away O₂ by simple cleavage (“reductive elimination”).

- 88) The term “daltonide” refers to the early nineteenth-century British chemist Dalton who was stricken in some arguments with colleagues like Berthelot on the constancy of compositions of chemical compounds, maintaining this position. Now also compounds are known, however, which somewhat vary in composition (e.g., Fe, Mn, Nb oxides) without changing crystal lattice structure or decomposing into a mixture of discrete phases (“berthollide compounds”). The term “daltonide” thus now is applied to denote a constant chemical composition of a compound or, here, of an entire organism.

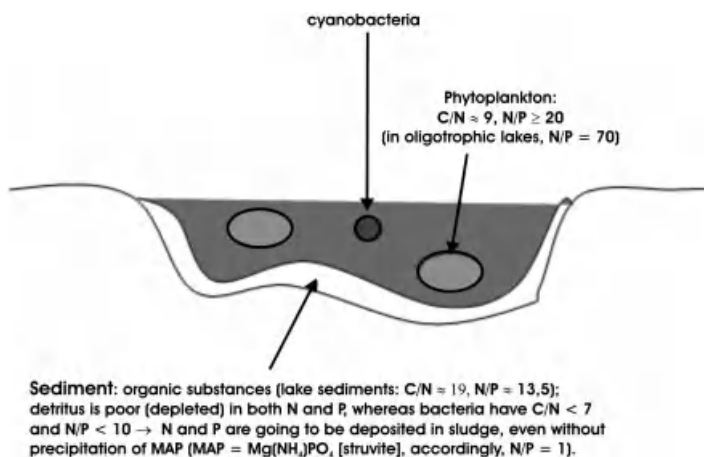


Figure 1.15 The variations among compositions of living beings in aquatic environments bring about either: (i) effective deposition of reactive nitrogen and phosphorus species in sediment or (ii) if precipitation fails, for example, for low Mg^{2+} levels, eutrophication

will occur even in the short run if atmospheric N is passed into the limnetic system by cyanobacteria (which contain and use nitrogenase) or by nodule bacteria in the rhizosphere of shore plants which are periodically inundated.

(here $x:y:z$ is to symbolize an undefined but rather general—and generally constant within a species or at least population—value of the stoichiometric ratios detected in biomass). Whenever living creatures are used in biotechnology to induce some matter transformations, these stoichiometric constraints will control the gross outcome; for example, it can be shown straightforwardly that in a sewage treatment plant the corresponding ecological stoichiometries of the involved microorganisms (include sulfate reducers in the CH_4 -forming unit) preclude any complete removal of non- N_2 (odd) nitrogen from the system, with some nitrate or NH_4^+ eventually turning up in open waters to which the cleaned sewage water is going to be discharged. Much the same holds for natural rather than constructed wetlands (Figure 1.15).

- a) Concerning the relationship between ecological stoichiometry and conditions of metabolism, it should be noted that the ratio C/N increases the more the weaker oxidants are at hand (Fränzle, 2010). Aerobic heterotrophs (animals, fungi) have $C/N \approx 7-10$, while in sulfate reducers $C/N > 100$. In clostridia—doing some pretty strange H transfer organic redox chemistry at the very end of the chances to get metabolic energy from “ordinary” organic compounds—it may even be 200 (in wood, rather than the entire plant, yet higher values are seen which cannot hold for an entire organism as its principal chemical building-blocks all contain nitrogen).

- 3) *Concerning metals*, which make up but some small share of an organism for most cases, the stoichiometric ratios are way less rigidly regulated and conserved than for C/N, C/P, or C/S. Given, however, that most of the actual content of essential metals is really needed to effect some biocatalytic transformations, and different metals are employed in different metabolic pathways (e.g., Mo in many oxidoreductases, Cu in hydroxylations of arenes, Zn in glycolysis), abundances of such metals should respond to metabolic changes much more than those of C, N, P do. When ambient oxidants like O₂, NO₃⁻ or SO₄²⁻ are removed, there is no longer a need to store and apply molybdenum, while requirements of zinc increase. Experiments revealed that common baker's yeast *Saccharomyces cerevisiae* does behave according to these expectations when forced into alcoholic fermentation, but it takes many cell generations to actually adapt in this manner.

1.5.1

Specificity

The specificity of elements in biology has several dimensions. First:

- Some chemical elements are best suited to effect certain transformations, then:
- Biochemical features will enhance uptake rates of certain elements in some organisms (hyperaccumulation, most often of nickel), moreover:
- This is related to essentiality insofar as—as a rule, rather than *by definition*—essential elements cannot be replaced maintaining the corresponding biochemical or information-processing (e.g., in nerves) function in a given species (exception see below), and finally:
- There may be elements essential only to certain closely related groups of organisms (I in vertebrates, Ba in desmid algae, W in clostridia, and some archaea), yet another dimension of specificity linking bio(inorganic) chemistry and taxonomy to each other.

Hence, unexpected uptake of some element might give a hint of its having some function, however, certain doubtlessly (for some living beings at least) essential ones are employed in just tiny amounts (V, and Co in man: just a few µg/day). As far as is known now, there is *no* chemical specificity meaning that some chemical element would just induce or take part in a single (thus, specific) metabolic transformation, rather, some are used again and again in functions which apparently could be accomplished more conveniently using something else (Fränzle, 2010). However, the inverse kind of biochemical specificity is there: one given transformation (most of which are related to transformations at organic carbonyl groups, plus hydrogenations) is promoted all over biology by the same element or functional group (if any): Likewise, peculiar enrichments of certain (i.e., non-essential) elements often are restricted to one or few species only.

1.5.2

Essentiality

Essentiality is defined as and proven by experiments which show a certain element or co-factor (“vitamin”) cannot be replaced or omitted in diet of some organism without compromising at least its ability to reproduce; as a rule, it rather will die upon prolonged depletion. The list of essential elements is illustrated in Table 1.5.

If all the elements are present yet differing with respect to the optimal intake, the scarcest one will control and limit growth and vitality of the organism regard-

Table 1.5 List of (almost) generally essential elements (there are some exceptions even for elements like Fe, while K often can be completely and reversibly replaced by Rb; Scott and DeVoe, 1954) (top), with the additions and some substitutions which hold for certain kingdoms of life and sub-classes thereof (e.g., cyanobacteria).

Generally essential elements

General	C, H, O, N, S, P, K, Mg, Ca, Mo, Mn, Fe, Cu, Zn
In higher plants	+ B, Ni
In algae	+ B, sometimes + Sr, Si, Cd, Br, I (discovery!)
In cyanobacteria	+ Co
In fungi	+ V, Na, Cl
In animals	+ Se, I, Na, V, Co, Ni, apparently As (V, Co, As in extremely small amounts), sometimes Cd; Na and K for information, osmotic purposes
In archaea	W replaces Mo; + Ni, Se

Elements involved in organoelement biochemistry

Halogens F^a through I, As, Se, Te

In metal bioalkylation: Tl, Ge, Sn, Sb, Bi, Cd, Hg, Co, Ni, Pt, Au

Daily demand in humans $\leq 1 \mu\text{Mol}$: V, Mo, Co, As (“ultratrace nutrients”)

- a) Although fluorine was already detected in bones, teeth, ivory by the beginning of the nineteenth century, soon afterwards also spotted in blood, saliva, eggs, urine (Emsley, 2001), this is no proof that it is actually essential (cf. cerium in bones). In fact, it still remains doubtful that there are growth or reproduction difficulties in humans or animals to be linked to fluoride exclusion. Further, NaF is used as a potent insecticide against cockroaches and ants, and fluorocomplexes of whatever metals tend to be the most toxic inorganic speciation forms of these metals around. The number of biogenic organofluorine compounds is much smaller than that of each of the other three nonradioactive halogens, possibly due to quite another mechanism of fluorination required (except with benzenoid hydrocarbons: V-dependent haloperoxidases might also introduce fluoride or nitrite to afford fluoro- and nitroaromatics, respectively; O’Hagan, 2006). The case is equally poor with purported essentiality of chromium: in metal complex antidiabetic agents it apparently is the ligand 2-picolinate [pyridine-2-carboxylate, an isomer of nicotinic acid (3-picolinate)] which is active, probably after reacting with some metal in the body, as it does not matter for medical activity which metal complex of 2-picolinate [Cr, V, Zn, Fe(II)] is administered and otherwise Cr is just known to inhibit enzymes.

less whether there are excesses of other essential elements at hand (Liebig's law of minimum; Liebig 1840). In some cases, actually replacement is possible for entire organisms rather than just enzymes [Zn by Co or Cd in some marine phytoplanktons (*Thalassiosira* spp., Price and Morel, 1990); K by Rb in many bacteria and algae (Scott and DeVoe, 1954; see above)], or there are alternative metalloproteins in the "genetic store" of a species for the same purpose [phosphatases using either Mg, or Zn or Mn, nitrogenases which employ V rather than Mo besides Fe (Eady, 2003), or carboanhydrases which replace Zn by Cd (although of different protein sequence and molecule size; Strasdeit, 2001)]. Here, if complete substitution of elements usually as crucial as Zn or Mo might occur (and it does in some cases), a "soft" definition of essentiality is required: take one out of several elements which likewise could be useful for the purpose but then in sufficient amounts!

What is *useful* cannot be generally inferred from what a technical organic chemist would apply to effect the very chemical transformation (even disregarding metal catalysts which are too rare to be of general biological use, such as platinum group metals, or Re): there are quite many differences even when transport and modification of small molecules are concerned (Fränzle, 2010). In addition, it can be shown that selecting one element which is optimal to effect one specific reaction (or two) during evolution (e.g., ruthenium in a hydrogenase) will be not supported over generations in biology due to very deep-rooted physicochemical (limiting) conditions of reproduction (Fränzle, 2010). These preconditions, not to be discussed here, then are going to limit the number of essential elements, anyhow being just some part of the not so rare elements (completely disregarding ones which are as abundant as Al or Ti), but also using some fairly rare ones (like V, As, Cd, W).

Organometal chemistry, the gentle art of making and transferring organic groups or molecules at, to or from metal centers directly, though being rather versatile also in aqueous or lipid media, is hardly used in biology except for some CO and ethylene complexes involved in acetate synthesis, signaling, and for Co [vitamin B₁₂ (*cobalamine*), binding and transferring C-based anions directly fixed to CO in different oxidation states] and Ni [construction of formyl (-C(H)=O) ligands and reduction to methyl, CH₄ at Ni of Ni porphyrines in archaea]. The purposes of metals and Si in biology are:

- Biocatalysis (enzymes), mainly transport and activation of small molecules (O₂ at Fe or Cu; CO₂ at Mg; NO₃⁻ at Mo, phosphatases which use each of Mg, Zn, Mn or Fe);
- Information processing (nerve membrane; Na, K), control of energy- and data processing (Zn, Mg);
- Signal detection (Fe₃O₄, ethylene receptor in plants, Cu), but not for obtaining optical or acoustic signals;
- Supporting structures (Ca salts, SrSO₄, SiO₂).

Supporting structures—in animals and aquatic algae more so than in terrestrial plants—require far larger amounts of metals or Si, P than the other modes of use.

1.5.3

Bioavailability

Of course, an element or compound can exert neither essential functions nor toxic effects unless being absorbed by the organism (disregarding the capacity of ambient or overlying UV absorbers such as ozone, metal ions dissolved in water to shield against UV phototoxicity which requires the elements, ions or compounds be located somewhere in the path of sunrays rather than absorbed by the very organism). By dissolving in nerve membranes and in the synaptic gap liquid, even inert gases (noble gases heavier than Ne; N_2 , CF_4 , SF_6) may influence Na or K ion passages, diffusion of acetylcholine etc. and thus become neurotoxic ("nitrogen narcosis" and other kinds of "rapture of depth" observed in diving activities; Bennett and Rostain, 2003). So, before estimating the risk of an element becoming toxic to a target organism or even be transferred yet further to offspring (by all deposition in eggs, transfer via placenta, nursing in mammals, some fishes and amphibia), one must determine whether and to which extent it is resorbed at all in a specific mode, also influencing possible damages [it is more risky to the central nervous system (CNS) to inhale mercury vapor than to ingest Hg^{2+} salts, let alone compounds of monovalent mercury].

As a rule, only some—usually even small—part of the spatially accessible (food, water, soil in rhizosphere) chemical elements are actually taken up by any organism (typically, 0.5–20.0%); in fact, limnetic trophic chains are distinguished by thorough concentration maxima in phytoplankton and then stepwise yet steady decrease of element (in particular, metal—both essential and non-essential) levels in the series of consumers (Reichenbach-Klinke, 1974; Fränzle and Markert, 2002a,b). As this is due to losses of elements as complexes both via the kidneys and across the gill interface (Figure 1.16), then augmented by complex-forming acids in the water, trophic chains in water are short, with top-level consumers either breathing air (thus avoiding the effect of metal leaching by gills in top-level consumers, e.g., whales, including river-dwelling dolphins, seals, crocodiles, but likewise ospreys or bears) or large fishes consuming plankton, other plants (whale and giant sharks, grass carps, etc.).

Apart from this, bioavailability depends on:

- 1) Speciation forms in the environment;
- 2) Species which interfere with the elements;
- 3) Local chemical conditions which influence resorption.

In case (1), some rules can be given: fatty tissues or plant oils tend to accumulate elements which form lipophilic speciation forms. This will hold both for non-metals the compounds of which tend to be covalent and uncharged (except for acids, oxoacids) and for metals, semi-metals if undergoing biomethylation while metal ions are hardly lipophilic, except for a few (especially Li^+ , explaining its role in neurophysiology), also when forming rather covalent carboxylates (divalent Be, Zn, Pb).

Typical and most important in case (2) is biomineralization. Sr, the heavier alkaline earths and Cd, Pb, rare earth elements are readily taken up and deposited

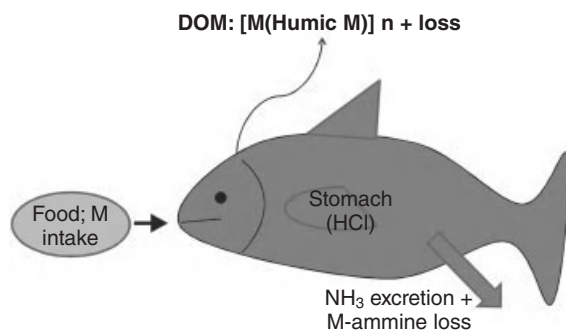


Figure 1.16 Intake and loss of elements around a fish. Ammine complexes will form and leach metals in the kidneys while organics dissolved in water (DOM = dissolved organic matter, including amino, fulvic and smaller humic acids, various nitrogen compounds) will cause extraction of metal ions from fish blood by complexation which occurs next to the gill membranes. When breathing water at a maximum dissolved O₂ content of some 10 mg/l (300 μM/l), a fish can oxidize at most 4 mg of organic (food)

carbon per liter of water passing the gills—and thereby releasing a few μg of the most abundant “biometals” to its own metabolism at most—will in turn pump all the external ligands dissolved or dispersed in one liter of water through indirect contact with its blood, so net loss along the gills is likely. In stomach, ingested, metals associated to protein- and other polymer-matrices are treated by dilute HCl, re-speciating some of them into chlorocomplexes (drawing by S. Fränzle).

alongside Ca in calcite or apatite biomineralizations, which among other effects enhances the uptake and subsequent in-body radiation doses of radionuclides like ⁹⁰Sr, ^{226,228}Ra. However, biomineralization depending on less abundant cations than Ca tends to be much more selective: SrSO₄ produced by certain marine algae contains appreciable amounts neither of Ca nor of Ba although the marine Sr/Ba ratio is not too large (about 500; Nozaki, 1997) and there are very considerable excess concentrations of Ca (Ca/Sr = 53 in Northern Pacific ocean water). Sometimes species from whatever kingdom of life accumulate elements without any reason to be seen: what will hickory trees do with rare earth elements (in particular, La) in their woody parts?

Generally speaking, bioaccumulation is a matter of both biochemistry (the chemical features which determine kind and strength of element–biomass interaction, starting with the peculiar chemistry of resorption in both autotrophs (from soil) and heterotrophs (from food and sometimes soil, water) and later being related to organ biochemical properties, and of the present speciation forms.

This is related to case (3): to start with the example which is both largest in dimension and most easy to comprehend, the alkalinity of ocean water (which is a buffer solution maintaining pH 8.3) causes most heavy metals to precipitate as hydroxides or carbonates. Hence dissolved levels of metals like Mn, Fe, or Cu are 1 nM/l or even less in seawater, and marine algae readily respond to Fe administration (ocean Fe²⁺ “fertilizing” experiments meant to enhance marine CO₂ uptake by photosynthesis). In freshwater, levels are four or five orders of magnitude larger.

Attachment of metal ions to soil polymers—humic acids and directly biogenic polymers from the organic soil fraction, including chitin, peptides—may block resorption as root-surface cells do not accomplish phagocytosis, as such large molecules or ions will not pass membranes by diffusion. Release is only feasible by metabolic decomposition—earthworms actually degrade humic matter and release compounds and elements attached to it, thus requiring peculiar protection ways to deal with heavy metals or As, Sb and so on. To avoid intoxication, namely, in-body precipitation of sometimes brightly colored sulfides (“do not eat yellow worms”). *Lumbricus* spp. earthworms containing As were found near a former As mine at Tavistock (Devon, UK); the latter is colored orange-yellow by in-body precipitation of As_2S_3 . Note that although As_2S_3 is very insoluble it is sensitive toward both O_2 and light (semiconductor photocorrosion), so the earthworm must cope with As, anyway as it will inevitably retrieve it upon humics digestion and it is re-mobilized in this aerobic organism if exposed to light. “Do not eat yellow worms” relates to the original title of a paper in *Nature* (Whitfield, 2003) where this first known case of sulfide precipitation inside metazoans—so far restricted to unicellular organisms like yeast—was described and discussed: bright yellow to orange refers to other As or Cd accumulation, while the even more toxic (Emsley, 2005) Sb will turn the worms dark red (and, with excesses of essential Zn an “innocently white” earthworm is obtained). For an earlier, more technical paper concerning adaptations of *L. rubellus* to just As and Cu, see Pearce *et al.*, (2002).

Besides degrading a matrix, bioavailability may also be increased by producing very efficient binding partners—such as hydroxamates, polyphenols or polylactons, cyclic peptides, particularly to sequester Fe^{3+} but also isocyanides in sponges (Simpson and Garson, 2004): when comparing which kinds of ligands are employed by bacteria, especially metallotrophic ones, yeast, and marine sponges to obtain or retain metals and transport after redox processes, one really wonders which are the primitive organisms given the simple compounds and procedures employed by both higher plants and also animals in gut resorption! Normally, in plants three or four different compounds are used to coordinate and resorb all the essential metals, save Na, K, Ca and Mo (about 7–10 left), that is, the ligands given away to the rhizosphere “must not” be specific in binding certain ions.

By the way, this non-selectivity, or versatility of metal ion ligation is also crucial for animals or fungi consuming plant materials: herbivory can only succeed, given the demand of animals and fungi for additional essential elements as compared to plants. Plants do not selectively absorb those elements which they need to run their own—autotrophic and thus more complicated—metabolism: a cow does “work” only due to plants using rather “primitive” ligands, and so does biomonitoring: Pb, Cd, As and the like could not be determined from analyses of plant or animal samples if they could not be co-resorbed “by mistake” (i.e., owing to poor cation–ligand binding selectivity). The above particular properties of bacteria, yeasts and other fungi in making highly efficient ligands have considerable drawbacks for rhizospheres in all since the latter also comprise such organisms in large amounts and biomass shares even if there is no specific mycorrhiza symbiosis:

ligands produced by the latter may mobilize metal ions in a manner that also allows for their (enhanced) absorption by plant roots around.

1.5.4

Toxicity

With every organism, there are elements, including some minimum set of metals (usually, K, Mg, Ca, Mn, Fe, Mo, Fe, Cu, Zn), required to maintain a number of biological functions, including:

- Catalysis;
- Information processing [not restricted to nerve membranes in animals but also covering, for example, the ethylene receptor controlling plant flowering and fruit growth/ripening, in which C_2H_4 gets bound to $Cu(I)$] and;
- Obtaining information (magnetite in bacteria, migrating birds, sea turtles and others).

In biocatalysis, often this function is related to attracting some substrate and/or a reaction partner of this by complexation and easing a chemical transformation by having it occur right within or next to the ligand coordination sphere. Of course, this kind of reaction critically depends on the “right” stabilities of complexes which combine all the substrates and the peptide/protein backbones which is also attached to the metal ion (and retains it within its polymer structure). Often, among chemically related elements like Be and Mg, Ca or most of rare earth elements/Tb the crucial difference between harmless or even essential and “highly toxic in general” just is that Be and Tb form too stable complexes (Figure 1.17).

Accordingly, an exchange of the central metal ion will, as a rule, disturb the balance among the involved compounds or ions or cause the products to remain attached to the center. Thus blocking catalysis (although there are some cases in which such exchange of metal ions in metalloproteins will even enhance catalytic activity, usually when Zn is replaced with Co^{2+}). Then, if another metal resides inside a catalytic protein, it is going to compromise biological function of this protein, producing a toxic effect on either the entire organism or some organs of it, thus, for example, causing infertility.

A telling example where a metabolic pathway which is quite common to different kingdoms of organisms is compromised by the same heavy metal ion in a specific manner (reaction mechanism), is synthesis of some porphyrine ring from aminolevulinic acid in all plants (Mg complex chlorophyll), animals, bacteria or fungi (Fe complex heme) which is commonly blocked by Pb^{2+} ions. Similarly Be^{2+} is highly toxic because it will replace Mg from crucial enzyme centers, and some carbamidinium salts and Tl^+ are (even more) so since transport of Na^+ ions by ion channels in nerve membranes is competed out, with these larger cations (tetrodotoxin, saxitoxin, Tl) sticking to the channels and blocking them.

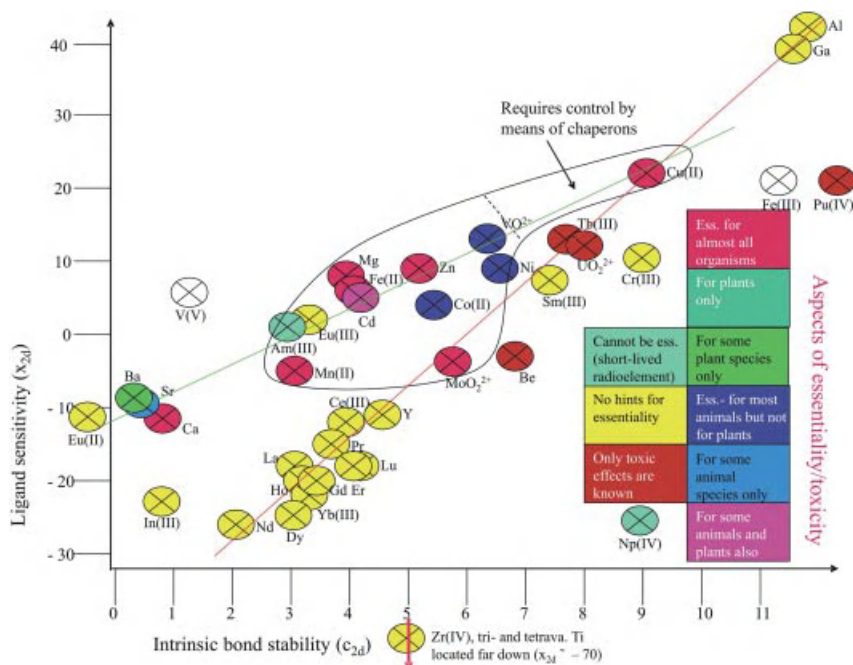


Figure 1.17 c_{2d} versus x_{2d} parameters of metal ions and essentiality. The exact values of c and x correspond to the crossing point of the lines inside the dot while the shadowing of this dot denotes existence and possibly range of essentiality (if there is any). While Fe(III) is absorbed by bacteria, it gets its biological functions mostly (exception: heme peroxidase) only after reduction to Fe(II); hence the symbol for Fe(III) is not colored at all. The actinoid elements U, Pu and Am are highly toxic but might be regarded either as radiopoisons or as chemical noxes. Both for uranium ($^{234,235,238}\text{U}$) and plutonium ($^{242,244}\text{Pu}$)

radioactive damages become negligible when compared to hazards by purely chemical modes of actions in the nuclides of longest half-lives (for those nuclides mentioned here: $10^5 \text{ years} \ll \tau_{1/2} < 4.5 \times 10^9 \text{ years}$) while there is no such isotope for americium ($Z = 95$; $T_{1/2} = 7400 \text{ years}$ for ^{243}Am , much less for all other isotopes); thus the different shadowing of the dots. The line which connects the essential divalent elements Sr, Ca through Zn, Cu follows a regression equation. Further information about this graph will be found in Fränze (2010).

By and large, the acute toxicity levels of essential elements do not vary in wide ranges, except for Mg, Ca which can be administered until getting close to causing osmotic disturbances [e.g., long-term ingestion of 5 g (!) Mg^{2+} /day apparently is quite safe]. Fe or Cu or Zn [with Cu^{2+} *usually* (not in every case!) causing violent vomiting upon excess oral uptake] are about as toxic as Cd or Pb (Emsley, 2005). An oral uptake of 200 mg uncomplexed divalent Fe will soon cause severe damage. Few elements are considerably more toxic (Be, Hg, Tl, As, Sb, actinoid metals—one can disregard radiotoxicity for long-lived isotopes) than the above, and Cd or Pb rather cause damages upon steady uptake over long periods of time; this is why

there are daily intake limits (e.g., 25 µg/day for Cd) more important in protecting people than the (relatively unspectacular) data on acute toxicity.

Metals usually differ from non-metals insofar as metal toxicity is less influenced by speciation, except for Cr or Sn, with dramatically increased toxicities often seen in organometal compounds if the latter are stable in water, including carbonyls. This actually is alluded to by the statement that “(heavy) metals cannot be degraded” – atoms of non-metals neither will “vanish” by chemical procedures but toxicities can be reduced more effectively in non-metals by changing their modes of chemical binding and/or oxidation states.

1.6 Information and Communication

Information, communication accompanied by re-considering the available body of knowledge and methods, contents of educating them is most important not only in pure and applied sciences but also in the realm of engineering. On regional, national and continental levels and across various periods of time, these are indispensable data required to understand and communicate especially environmental problems (Markert *et al.*, unpublished data).

In order to improve accuracy and sensitivity (lower thresholds of detection, detection of chemical species which hitherto escaped analytic procedures) of analytical techniques and measures of environmental technology issues of precision, reliability and reproducibility of certain methods gained ever more importance during the last decades (see Sections 1.4.1.3–1.4.1.4, 1.4.2.2). There are relationships and interdependences among information, communication and reflection on contents which were outlined recently (Markert and Fränzle, 2007; Markert, Fränzle and Tieben, 2009). Results of these considerations presumably bear fundamental implications for advancing emotional and rational, as well as technical (artificial) intelligence by education policies and bring about a novel process of education by dialog (Section 1.6.7).

In colloquial terms, communication is an exchange of information, describing a topic and activity which in itself contains (at least) two key issues:

- First, what is correct or wrong information, how can I produce or reveal it, respectively, proving the quality, that is, accuracy of information.
- Second, how and by what means can information be distributed and spread, giving everybody the chance to access and retrieve it regardless of its origins and contents.

One thus is posed to ask for issues of quality and principal meaning of information and its transfer for an advanced society, also regarding the risk of information being manipulated on its way. In the long(er) run, problems and paradoxies encountered there can best be tackled in the framework of “dialogical education” processes (DEP).

1.6.1

What Is This Thing Called Information?

Processing and transferring information now is crucial for achieving a sustainable, high-level way of living, besides addressing the problems related to use of matter and energy (see Lubchenco and Mehra, 2004; Huntington, 2000; Patrinos and Bamzai, 2005; Rosnay, 2000; Tiessen *et al.*, 2007; Walker, 2006). Information means to convert hitherto unknown into established knowledge (the Latin verb *informare* means to educate, to give things some shape). Recently these pieces of information is “encoded” by certain symbols or formulas, with humans made familiar with those codes in cultivated societies by explicit and lifelong learning, including professional education and personal engagement.

Figure 1.18 is to show how information is gained in a stepwise, open but never really completed multi-stage process (Roots, 1992). As a rule, measurements and other kinds of observation produce some set of data, thereafter selecting some of these data to obtain specific pieces of information and finally knowledge and recognition (Nefiodow, 1999). If the things thus understood can be judged about also in the later future, both the individual and society end up with a generally valid, secure plus of knowledge.

During the (so far) last steps of evolution, this way and process to gain knowledge at increasing pace was due to the vast (size and complexity) growth of the neocortex in anthropoid primate brains, with culture and learning by trans-

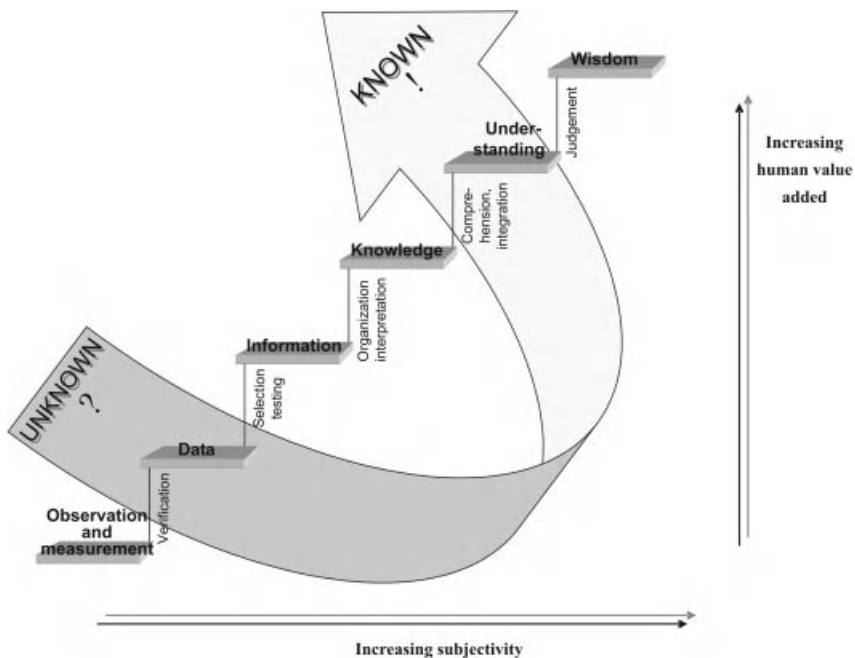


Figure 1.18 The staircase of “knowing”, modified after Roots (1992).

generational tradition (by parents, kindergarten, friends, school, etc.) giving mankind an immense gain of knowledge which is going on, now secured (by both acquisition and storage means like writing, electronic storage) and which provides the decisive competitive advantage among societies (Miegel, 2005; Biedenkopf, 2006; Kirchhoff, 2006).

Within about 100 000 years,⁸⁹⁾ humans developed patterns of thinking and acting which permitted a most successful spreading across continents almost all over the Earth. Using education in a skillful and intelligent way—that is, selecting and applying solid pieces of knowledge—renders education the principal and crucial factor of future life (Hosang, Fränzle and Markert, 2005; Markert, 2005).

For millenia now there has been another pathway of information besides scientific and rational investigation of our environs by (producing) information and knowledge, that is, religious beliefs (Figure 1.19). Lieth (2005) coined a term to distinguish between the levels of knowledge based on ratio and faith based on spirituality, namely telling apart real versus virtual information.

It has been shown several times that pieces of information belonging to (either) empirical knowledge or faith must be precisely and meticulously separated (at least here in the secular Western world), yet the gain of information and knowledge obtained by either path—empirism and faith—does not differ too much (Küng, 2005; Markert *et al.*, 2006; Ratzinger, 2006). Both faith and knowledge are rooted in pieces of observation, experience and hypotheses which are maintained only until they got clearly falsified (Popper, 1957). Hence one needs to ask and get criteria whether some piece of information is reliable (“correct”) or wrong, prompting us to consider the ways in which information is actually processed.

1.6.2

Information Processing and Communication—The Ratio and Relationship between Subjective and Objective Factors in Processes of Recognition

Hypotheses can never be “verified”, finally called “true”, not even in natural sciences, because during the development of man and mankind regularly completely

89) The notion that the spreading of modern humans all over the Earth (except Antarctica and southern parts of South America) took just a few thousand years is erroneous. Leaving aside the fact that *Homo erectus* did the same much earlier [being present in Spain, Georgia (Caucasus; Dmanisi excavation site) and Indonesia (Trinil on Java, next to Flores where the last *H. erectus* might have survived until a few centuries ago) >1 mio. years ago, later also in China (“Beijing man”) and Central Europe], the first few (tribes or individuals of) *H. sapiens* started to migrate off Eastern and Southern Africa some 200 000 years ago, to arrive in the

Middle East more than 100 000 years [Qefna cave, Israel (Mount Carmel)] ago, making it to Australia some 60 000 years ago and to northern America 13–15 millenia before now, about the time of onset of agriculture (“Neolithic revolution”) in both north western Asia (Anatolia) and the lower Mekong area (Vietnam, Cambodia). So the average speed of “migration” of *H. sapiens sapiens* to new territories was about 100 m/year, a group or tribe would thus as a rule not completely relocate “its” area required for hunting and gathering completely within a generation’s time, except when passing open ocean. See also Table 1.1 (Section 1.2).

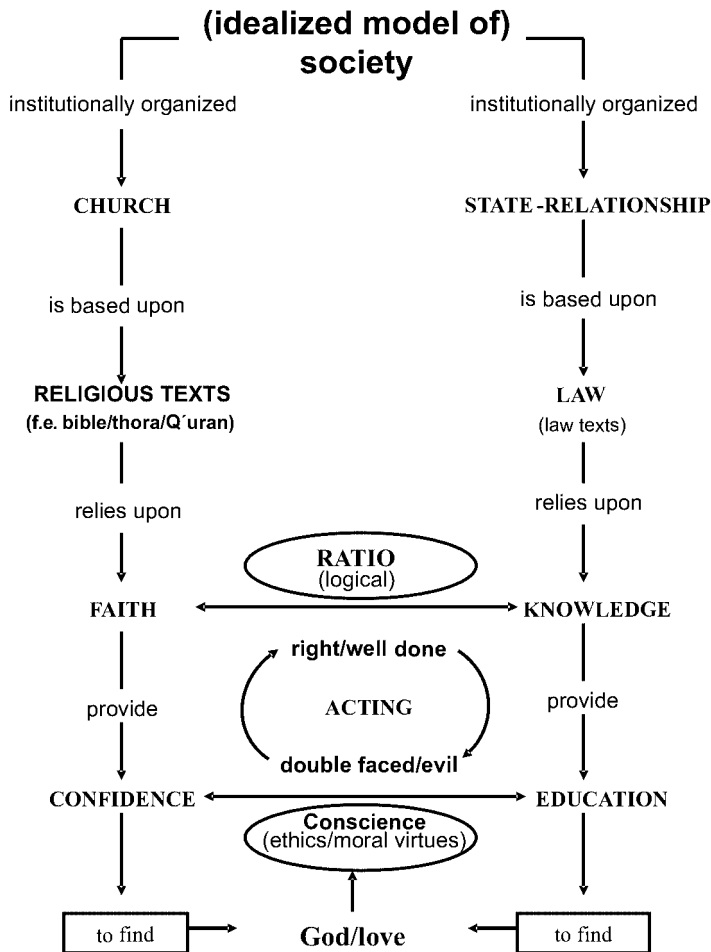


Figure 1.19 An idealizing model description of structures of society: the upper half is constructed by institutions including church(es), religion, state and law, while the lower—cultural—part is supported by faith, confidence, knowledge and education (taken from Markert, Fränzle, and Hosang, 2005). Convincement is brought about by linking

ratio (logical thinking) and conscience (ethics, moral) in a dialogical manner to separate right from wrong and good from evil. Self-confidence and education find their way into people loving each other, considered to be the only acceptable ends of society which may be negotiated. For additional explanation, see text.

novel developments and recognitions occur which were by no means anticipated and require steady renovation and re-consideration of things so far thought and supposed (Popper, 1957). In addition, there are fundamental problems from information (transfer) theory (Shannon and Weaver, 1976). Thus something now still considered “established knowledge” may tomorrow be falsified by experiment and hence dismissed as nonsense.

For example, in the nineteenth century physicists were quite convinced that atoms would not (inter-)change. About 1902 the reasons of certain anomalies in chemical reactions taking place involving highly radioactive samples became obvious, namely that, chemical elements in such conditions would not remain what they were (Becquerel, 1903) and correspondingly might behave differently next morning (Segre, 2002): they could spontaneously convert into each other, changing chemical behaviors⁹⁰⁾ also. Another rather dogmatic view—which, however, was challenged much earlier (mid-nineteenth century)—of similar kind was that biological species were constant, eternal—except for extinction—and not going to change anyhow. Now we know that organisms of all kingdoms are subject to constant development (or, rather, change) and that evolution is dynamic (Fränzle and Markert, 2006). A misinterpretation of some theoretical concept (Lewis's octet rule), combined with experimental difficulties, tempted chemists to believe the existence of (covalent) noble gas compounds to be impossible. Strangely, corresponding experiments in the xenon–fluorine system (Yost and Kaye, 1933) provided no isolable compounds, although both XeF_2 and XeF_4 (xenon di-, tetrafluoride–noble gas compounds) must have formed then and attempts made to intercept them with sufficient precautions (cold fingers) and so on.

In a sustainable information- and knowledge-based society, it is crucial to provide reliable answers concerning “right or wrong”, “subject to lie, manipulation or improvement”. In national economics, sound data on population development, unemployment rates and many more are indispensable.

Many citizens now doubt increasingly concerning an increasing number of topics, including wartime reports, environmental and economic data, whether there is any “truth” in those lots of pieces of pertinent information from most diverse sources, comparing it to their everyday experience, and finding it to be too “beautiful”, too optimistic or simply too positive (or else, negative). Nevertheless, published sets of data are the principal starting-point of any planning and making decisions for one's own future, and that of one's own children, arguments and methods must be found to estimate whether some purported “fact”, case or relationship is probably likely or rather unlikely; otherwise there is no foundation anymore to have matters settled by discussion and arguments. The way outlined here is mainly related to Markert, Fränzle, and Hosang (2005).

Objectivity and accuracy of information, so it has to be acknowledged, cannot be achieved on any arbitrary level of data aggregation, and hence data, opinions, predictions and their likelihood of being realistic depend on this very aggregation; it is pointless to demand objectivity if this aggregation level does not match, and in addition it must be considered when (or from which point onward) subjective

90) Conversely the concept of isotopy was developed about the same time (1911) when the nucleus of atoms was discovered: now there was a grouping of (itself radioactive or, rarely, stable) entities of very similar chemical behavior, now (from then on) considered all to be some kind of

lead or bismuth or radium and so on, regardless of what they had been or isolated from before. This approach eventually brought about the discovery of nuclear fission (Hahn and Strassmann, 1939).

feelings and opinions influence construction of an “objective” point of view once more. For explanation let us re-consider the stage model of Figure 1.18.

Observation and measurement produce data which then have to be subjected to statistical evaluation and selection eventually to become pieces of information. The validation of information thus obtained, combined with or done by interpretation and linking to already known facts, reorganization and coordination, turns information into knowledge. If density/amount and integration levels of new knowledge with “old ways of thinking” suffice, this process provides better understanding of matters hitherto investigated, with the knowledge to be stored for further use in libraries, electronic storage systems after multiple objective checks. So the steady increase of our knowledge should bring about some better understanding of phenomena.

As can be concluded from that stated before, understanding and proper use of information and knowledge imply some subjective judging of pertinent facts which—at least on a short term—is at odds with rational arguments and logical derivation. The ability of both individuals and social entities (groups) to learn, that is, to accept and process new observations, measurements, data, pieces and eventually knowledge continuously, is called “education” here (see Markert, Fränze, and Hosang, 2005).

Accordingly we must accept that “pure objectivity” of data and statements is constantly decreasing up the “staircase of recognition” due to increased levels of aggregation. Objectivity diminishes with an increasing share and extent of single events/observations and linkages among them, producing relationships which are to be subjectively judged and viewed upon simply because “objective” measurement or reproduction are no longer feasible. What, then, is correct or wrong, true or false?

1.6.3

Ways of Producing Knowledge Established in Natural Sciences Lead Us Back to Accepting and Integrating Plurality of Views and Opinions

Recognition in natural sciences does regard subjective, even somehow speculative opinions and perceived facts as “true” (i.e., working hypotheses) as long as the opposite was not demonstrated. In fact, this process of collecting and formulating different opinions is called formulation of hypotheses; in this framework production of new hypotheses—including speculative ones—is accepted until they are falsified, exposing them as untrue.⁹¹⁾ Thinking in natural sciences thus disallows straightforward elimination of some—even apparently absurd—opinion before checking the underlying facts. And this is good, because it avoids an all too early elimination of unwanted approaches from discovering facts or alternatives for technical solutions in natural sciences like it might happen so often in (areas

91) Statements which cannot be falsified owing to their content or formal shape at all, are not considered true but rather non-scientific, let alone hypotheses. You

must distinguish this from axioms which likewise cannot be formally proven or disproven (falsified) but are useful in heuristic terms.

similarly exposed to) public opinion. In natural sciences, it is much more difficult to control opinions by forming lobbies than with a parliamentary debate. By providing a serious method of falsifying hypotheses, rather than premature dismissal of ideas and thus likewise protects “minorities” from being put aside and discredited too early.⁹²⁾

However, if this attitude of tolerance toward different opinions would be maintained generally, it would be hard to raise some democratic majority to tackle a practical problem or issue; accordingly asking for “right or wrong” at least at the base levels of data and information is required.

Telling what is “right or wrong” apparently is a task for law scientists, judges, attorneys, and members of the domestic secret service. However, also fundamental decisions in law are possibly flawed and thus doubtful for the very reasons given above, results from exact natural sciences shall be used to describe the way toward established knowledge. In analytical chemistry, concerned with methods to determine “what is present or absent”, the situation is very much like that what is to be done first in any serious analysis of society: doing a serious analysis of the present situation at first (Miegel, 2005).

In both analytical chemistry and all related branches of natural sciences there is a clear distinction between two terms, namely accuracy (rather corresponding to “truth” in law terms) and precision which just means that repetition of the experiment yields about the same measured data (in politics corresponding to social moods, opinions or trends; Figure 1.20).

Correct analytical results (statements of other kinds) cannot be produced by “democratic majorities” among a manifold of similar results (Griepink, 1990) but require rigid control protocols, like use of standard reference materials and mutually independent different ways of analytical measurement, making accuracy and “truth” of the obtained data most likely.⁹³⁾

The latter statements imply that terms must be used conforming to a common content before putting them into a wider context.

To give an example, take the terms “knowledge” and “belief” which used to be separated without much prior consideration into a pair of opposing views on the world, one which is based on objective experience and the other on some kind of transcendent religious statements. Doing modeling and applying systems theory

92) We are fully aware that this (critical positivism) is somewhat idealizing the way knowledge is gained in natural sciences. Max Planck once stated, bitterly, that there is no way to convince people in the path of revolutions in exact sciences but you have to wait for the proponents of the old position to get biologically extinct; this actually has a fundament in history of sciences, with Planck himself and Sommerfeld being the only prominent physicists born much before 1880 who eventually “accepted” and adopted

quantum mechanics, and H.A. Lorentz (1853–1928) “resorting” to electrodynamics and the basics of special relativity. It is just a historical exception when there are creative phases of just trying what can be done with a novel device or formalism (e.g., quantum mechanics during the 1920s).

93) This is not the place to discuss protocols of quality control in analytical chemistry in more detail; rather we point to corresponding textbooks.

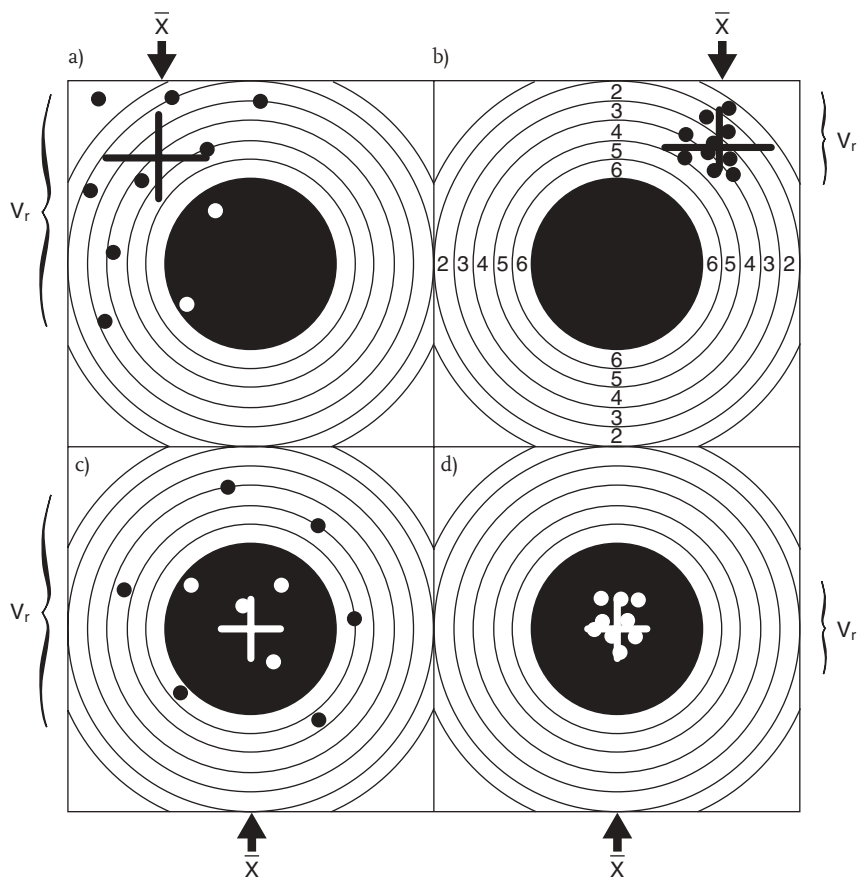


Figure 1.20 Illustration of the terms “precision” (reproducibility) and “accuracy” (the “true” value) in analytical chemistry (after Toelg 1976 from Markert, 1996): (a) Poor precision and poor accuracy, (b) good

precision and poor accuracy, (c) poor precision and good accuracy, (d) good precision and good accuracy, $\bar{x}$ = arithmetic mean, ν_r = coefficient of variation.

to these terms shows, however, that either category relies on identical approaches, models and methods, producing common features and modes of behavior for in-group communication. Natural sciences rely on observation, experiment, but also prior experience and make use of knowledge produced and published earlier. Some biological phenomenon, for example, gets described, documented, possibly corroborated by some laboratory experiment⁹⁴⁾ and cast into some hypothesis. This hypothesis will be around until being falsified by another scientist. However, it often happens that scientist2 obtains some other results which are not at odds with hypothesis1 and thus can co-exist with it. Another scientist3 adds yet more

94) Biochemistry, behavioral experiments, birds flying in a wind-tunnel and so on.

non-contradictory material to this and thus a pluralistic scientific community is created which cares about keeping opinions and meanings of terms objective. Of course this is no way of “moral quality control”, with this protocol both enabling, e.g., military abuse of scientific knowledge and tremendous achievements of human societies covering most diverse areas.

Now extend the above approach to faith: every religious statement, topic of faith can be verbalized, hence described, compared to others and possibly corroborated—or contested—by some experiment (see the manifold of scientific investigation on the Turin shroud). Even after this, the individual is left with “faith” as a kind of hypothesis that he (alone) has to maintain, by believing. People believing in something else do the same . . . One result was construction and stabilization of the five large world religions. These—like natural sciences—did achieve “incredible” things. However, wars “legitimated” by religious arguments or “God’s will” had and still have disastrous consequences.

1.6.4

Examples from Environmental Research

In biological systems, information does not just exist as genetic information only, but also includes chemical signals (compounds which carry information) which serve this purpose both within one organism (hormones, in animals also neurotransmitters) and among them, chemical signals which are produced by organisms and biocoenoses in metabolic activities which alters the respective environments, enriching it with certain substances while others are depleted. An exudate of the roots of a certain plant species can inhibit seedlings of another species from growth in the immediate vicinity. Conversely, this kind of information brought about by locally limited chemical effects and changes can also construct commensal relationships and even outright symbioses, causing one partner to settle where corresponding chemical signals do exist. Helmut Lieth once asked “how much information there is in a meadow”: answering this question includes to understand how organisms shape and structure their next vicinity, and (how) they do this by chemical means. Both horizontal and vertical, plant societies are rather diverse on decimeter scales, contributing much to the amount of chemical information,⁹⁵⁾ controlling the pathways and actors of succession by controlling which plants and animals can colonize some site only after corresponding changes of site and geobiochemistry (soil formation, changes in recently formed ponds, biochemical weathering and sediment formations) took place. The newly accessing organisms, of course bring about their own, literally specific, chemical and genetic information. Ecotones are key to such spatiotemporal processes because they

95) Chemical taxonomy of plants has it that related species share common products of secondary metabolism, including alkaloids, which can thus prove their being related. However, closely related species are unlikely to coexist at one site (competitive

exclusion principle), and mono-species areas are highly unstable. Hence, there is a trend toward high diversity of secondary metabolites in a rather stable plant community.

link different ecosystems and biocoenoses over steep chemical gradients (e.g., in a lake shore).

Moreover, there is a thermodynamic entity, namely entropy, which describes either the extent of disorder or the likelihood of spontaneous formation of some systems state. Entropy corresponds to information and reveals what are the limits of information passed along a certain channel over time (Shannon and Weaver, 1976): a state which can be produced by “shaking” some array of items, that is, by undirected modes of perturbation, is poorly ordered, distinguished by high entropy, however, low information (density). Biological systems are capable of introducing highly ordered states to both themselves and their immediate environment but only by exporting entropy and/or uptake of either electromagnetic (light, in photosynthesis) or chemical energy. Formation and spreading of biological information (reproduction, shaping of biocoenoses) inevitably includes destruction of other biological, biochemical or chemical information which, for example, happens during digestion. Metabolism thus brings about a spatial relocation of information, producing an inward (into the organism) flow of information. Accordingly such an active—which simply means: living—organism can be considered a transfer channel of information (to use Shannon’s term), much like a telephone cable, and the rules of information entropy handling apply.

Shannon’s classical treatment considers “white noise” as the outcome of information entropy production which eventually limits the transfer capacity of any single information transfer channel. In real environments, besides noise there is another limiting factor, namely the conditions required for growth and reproduction of present organisms. Here is a difference in effect between biodiversity and net metabolic productivity which both are used to describe a biosystem but are not directly related with or dependent on each other. Formally (high) biodiversity causes a(n increased) flow of information through an ecosystem which, to a first approximation, is proportional to the number of involved species⁹⁶⁾ while the number of individuals per species and generation period means informatory redundancy in Shannon’s terms (Shannon and Weaver, 1949), increasing information flow just by the logarithm of the number of individuals.

Accordingly, even small changes of biodiversity cause larger changes of information flux through an ecosystem than are effected by (even substantial) changes of its (net) productivity. Biotopes which are poor in nutrient- or energy supply (arctic areas) in both land and ocean are distinguished by a small number of species which however may occur in tremendous numbers, whereas tropical ones (regardless of severe nutrient limitations in coral reefs or Amazonian hylea) usually contain very many species, although net productivity likewise may be low. The latter kinds of ecosystems bring about a very large flux of information, with small redundancy (small number of individuals per species) causing larger decreases of information flow if one species is extinguished locally. The upper

96) “Species” here denotes a group of organisms which are a potential reproductive community. As reproduction is the key pathway for this information under consideration, the above species definition—which in biology is rather restricted to animals—does apply.

limit of information flow through one information transfer channel is given by Shannon's theorem.

Due to their very being signals, chemicals which are used in information transfer (e.g., hormones) also bear information beyond that encoded in their chemical structure. In metazoans there may be exogenous signals taken up from a polluted environment [as simple as NO (nitrogen monoxide) or highly complicated, like synthetic steroids or neuro-/psychoactive drugs], leaving the "informed" sub-entity (e.g., a cell or an entire organ) incapable of distinguishing whether these signals come from some other part of the same body or from outside.

As a result, there will be wrongful information processing, spelling deformations (action of teratogenic compounds, cancer), miscontrol of metabolism, loss of fertility and further deviations which may be lethal themselves or jeopardize some local population. Environmental chemicals, including phenols which bear the key structure motif of estrogens, halocarbons like 4,4'-dichlorodiphenyl trichloroethane (DDT) or PCBs and triorganotin compounds all are capable of causing sterility and genital malformations in mollusks, fishes, ice bears and reptiles. Although the annual consumption of steroids like 17-ethynylestradiol (EE₂) appears to be very small (some 50–60 kg/year in Germany), a simple calculation considering the annual total rainfall in Germany shows that even on average the biological action threshold for sensitive limnetic organisms (0.3 ng/l) is almost reached, in densely populated areas it will be considerably larger than this as sewage treatment plants will not remove it.

1.6.5

Performance of Brain and Modern Computers; a Comparison—Artificial Intelligence and the Internet

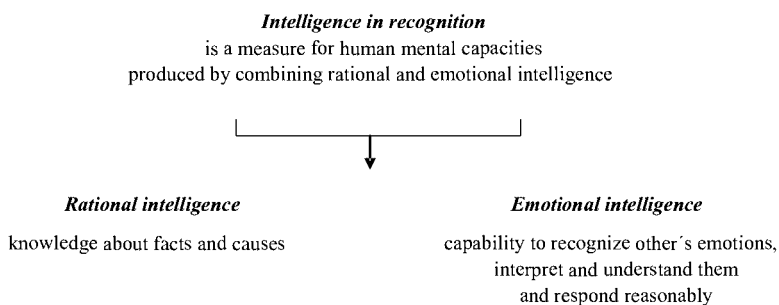
Regardless of the enormous progress in research on cerebral and neuronal functions of both morphological and physiological kinds which was achieved by medicine and natural sciences alike the tremendous complexity of the brain limits what is known about brain performance and its exact mode of control. Accordingly, the actual performance cannot be estimated either. While the human brain contributes just 2% to body mass, it takes more than 20% of oxygen demand. Because the brain is so active and too small to store substantial amounts of either oxygen or energy [glucose, nucleoside triphosphates (NTPs)] even rather short interruptions of blood supply can cause severe and irreversible damages of the brain. The total length of all the nerve fibers and axons inside the brain is estimated to be 5.8 mio. km, that is, 145 times the length of the Earth's equator (<http://www.de.wikipedia.org/wiki/Gehirn>).

Information processing occurs on a molecular level, starting with membrane-dependent potential differences which can be measured, up to (e.g., neuromuscular) the activity of the entire organism. While elucidation of molecular and biochemical mechanisms, down to their details, may be the everyday business of physiologically oriented neurologists, larger complexes of brain research, especially in description of specific cerebral processes, remain topics of present and

ongoing research. These topics include electrochemical interactions [what do electroencephalographs (EEGs) cause and tell?] and how far the brain consciously controls (by feedback) activity of entire of its centers, being in the center of recent research strategies and aims.

Often comparisons are made between the processing power of the human brain and that of the most modern computers. The brain is estimated to execute some 10^{13} to 10^{16} analogous process steps per second, as compared to 4.78 times 10^{14} floating point operations in IBM Computer Blue Gene/L (470 teraflops). The high performance of the brain is achieved by its many parallel operating connections among neurons rather than a high speed in doing single steps. While parallel architecture is common to the brain and high-speed computers, a biological (neural) network acts simultaneously as storage- and processor logic devices, which are separated in computers. This allows to re-new the entire storage content of a neural network during every single step while computer must and can only do this actualization step by step, that is, slower.⁹⁷⁾ One specific domain of informatic sciences is called artificial intelligence (AI) which strives to copy, reproduce and automatize “intelligent” behavior. The branch of strong AI tries to simulate and replace humans by constructing a kind of intelligence which thinks and solves problems like man does, being endowed with consciousness, self-consciousness and even emotions.

In spite of lots of corresponding attempts there is apparently no research strategy which promises to be successful into this direction. Rather, there is a recess to weak AI which means simulating intelligent behavior by making use of mathematics and informatics. Here, neither creating non-biological consciousness nor a deepened understanding of what makes intelligence are in the focus of interest. There are different forms of intelligence (not to mention the business of intelligence agencies . . .) which ought be defined as follows at least for the purposes of this volume and the forthcoming discussion (Figure 1.21).



Artificial intelligence is a technical product feature, e.g., computers and roboters may be endowed with by humans, which is accomplished both by peculiar kinds of software and by using sensors informing the system about its environment.

Figure 1.21 Simplified definitions of intelligence used in this volume.

97) (<http://de.wikipedia.org/wiki/Gehirn>).

Computers used for such purposes are called expert systems. Expert systems rely upon some data bank which stores specific pieces of knowledge. Hence the system is capable to tackle complex problems, cooperating with humans using it. Here it shall be investigated which are the conditions in which computers can mimic modes of behavior which would be considered intelligent behavior in living beings.

The internet, being an electronic network which connects smaller computer networks to provide fail-safe connections among “individual” computers for exchange of data. There are programs (algorithms) to retrieve specific data according to keywords or even verbalized questions. The recently best-known of these agents is Google, having a share of 83–90% in the German-language Internet. Google offers important pieces of information, representing all text files, pictures and videos, plus “free of charge” e-mail services and translations of foreign-language text files. However, Google also screens these e-mails for certain keywords and then abuse corresponding pieces of information for personalized advertizing. For example, when the term “car” repeatedly occurs in your personal mail traffic, you can expect to be hit by car advertisements in your mailbox.

Of course this raised criticism against Google for years (Bergere and Osmont, 2007), concerning not just the safety of personal data but also the issues of author’s rights.

In April, 2007, Google purchased the online advertisement firm DoubleClick, rising concerns among competitors because Google was already number one concerning text advertisement in search results, now possibly heading for a monopoly. DoubleClick⁹⁸⁾ now offered Google the pole position in online advertisement using pictures and videos also. Hence not just competitors in online businesses but also civil rights groups objected to this takeover at the United States Federal Trade Commission. Concerns on data privacy are caused by the protocols producing lots of data on individuals’ surfing behavior, data retrieved by both DoubleClick and Google. Personalized online advertisement just may be a nuisance but these data can as well be sold further or otherwise misused.⁹⁹⁾ Microsoft tries to compete by hostile takeover of Yahoo, investing some US \$45 bio.¹⁰⁰⁾

1.6.6

Emotional Intelligence

Intelligence as discussed refers to cognitive abilities akin to the neocortex which mainly supports logical thinking and acting.

Already in the late 1960s Joseph Weizenbaum, then with the Massachusetts Institute of Technology (MIT; Boston, Mass., USA), wrote the “Eliza” program to simulate the way psychiatrists talk to their patients, permitting the illusion of communicating to a real, human, soul-bearing speech buddy. Weizenbaum himself was shocked to learn the actual effects of this fairly crude program on humans—both psychically healthy and labile—and soon turned from a pioneer of

98) (www.doubleclick.com)

99) (<http://www.heise.de/newsticker/meldung/88379>; <http://www.heise.de/newsticker/meldung/90306>).

100) (<http://www.spiegel.de/wirtschaft/0,1518,532565,00.html>).

artificial intelligence (AI) to a critic of computers and electronic media (Weizenbaum, 1978).

During the past few years scientific research became focussed to another brain structure and kind of intelligence, called “emotional intelligence” by Goleman (1997). The structures which process the corresponding information are sited very deep inside the skull.

The cognitive brain—associated to the carved surface of neocortex—supports cognition, speech and thinking, whereas the emotional brain controls our personal emotions. After the emotional and cognitive parts of brain acquire some information from outside next to simultaneously, they can either cooperate fruitfully or compete for control over thinking, feeling and behavior (Servan-Schreiber, 2006; Schmid, 2008). Whether cooperation or competition prevails in this interaction determines our feelings and our attitudes toward the world and other people. With competition and “rivalry” prevailing, we feel bad and uneasy.

If, however, the emotional and cognitive brain support each other—with the emotional one shaping our life while the cognitive causes us to advance in this very direction prudently—we notice inner harmony, giving the foundations for long-term well-being (Servan-Schreiber, 2006). Because the brain is rather flexible, with different parts involved in certain functions, hence we cannot visualize states of either cooperation or competition among different brain features by optical methods. Nevertheless in some cases both deep and particular harmony acquired by meditation or effects of psychical diseases including severe depression may show up in anomal increased or decreased activities revealed by such methods.

Besides increasing the psychological contribution to healing people these works strongly influence cognitive psychologists (Gigerenzer, 2007), including research on effects of modern media on humans (Kast, 2007). Making use of this novel “emotional medicine” gives a chance to treat modern psychological mass illnesses such as depression, fear of future or stress to some extent without resorting to either medication or years of psychotherapy (Servan-Schreiber, 2006), as the “emotional brain” is in charge of many body functions and the corresponding parameters such as rhythm of heartbeat, blood pressure, hormone levels, functions of digestion and immune systems.

A very peculiar work deals with so-called savants, that is, people who, although often cognitively impaired, yet achieve extraordinary performances in some very small specific areas. Some 50% of the (rather few) savants are autists. The movie “Rainman” by Barry Morrow (script) was inspired by the actual life of one savant [although Kim Peek (1951–2009) was not an autist]. While savants apparently lack pronounced emotions, they can be capable of fantastic memory performances, including historical facts, or be remarkably creative in producing thoughts along uncharted ways (Einstein effect¹⁰¹).

101) Einstein himself probably was neither an autist nor a savant, being both highly emotional (although difficult in his most personal relationships) but fellow physicist P.A.M. (Paul Adrien Maurice)

Dirac (who theoretically conceived antimatter) and philosopher Ludwig Wittgenstein are now considered to have been suffering from rather severe forms of “autism-spectrum disorders”.

1.6.7

How to Shape Dialogic Education Processes (DEP) as a Future Principle of Communication

One needs to develop some generalizing concept to conceive a pathway into some information process which is all economically reasonable, ecologically responsible and maintaining peace between nations and societies. This concept requires to be theoretically sound and applicable to the economy, yielding the corresponding effective information and improving the present situation.

By now, correct information from economy, environment and social living conditions are not delivered to the majority of people in the World and, moreover, lack integrative reflection (Markert, Fränzle, and Hosang, 2005; Markert *et al.*, 2006; Tiessen *et al.*, 2007).

For example, Chinese citizens—some 20% of all mankind—are kept from uncensored access to Internet; additional billions of men cannot afford it. Is a “war for education” imminent?¹⁰²⁾

Needs and demands can no longer be met on the scale of entire (though still affluent) societies in either Germany or all of Europe. This once again calls for a concept which takes equal regard for the specific conditions and demands related to cultural history and the individual. Therefore, research on intelligence has to integrate cognitive and emotional processes of information.

Figure 1.22 depicts a scheme which combines multicultural common positions and parameters from natural sciences into a line along which “dialogical education” might arise and grow with time.

People of most diverse backgrounds need a common code of values and education which likewise regards individual demands and obligations toward society. Intelligence apparently includes a peculiar ability to produce relationships among different sources of information, with love and power being at odds ever since. While love (for yourself, for others, for nature) is in favor of positive relationships, power can be abused and thus promote negative relationships (Janisch, 2007).

The distribution and processing of information in this broad sense are and will remain crucial to analyze and understand whatever processes in environment, economy, and society. So-called “quasitruths” will vanish in the long term. Goudevert postulated years ago that “technical education without general education tends to produce knowledge without conscience”, introduced to us in Section 1.7 “Ethical aspects for society”, following Markert (2003).

1.7

Ethical Aspects for Society¹⁰³⁾

While a globalizing society increases both its level of complexity and body of knowledge faster than exponentially (see Section 1.6), rapidly ongoing events and

102) (<http://www.laptop.org/-index.de.html>)

103) According to Markert (2003).

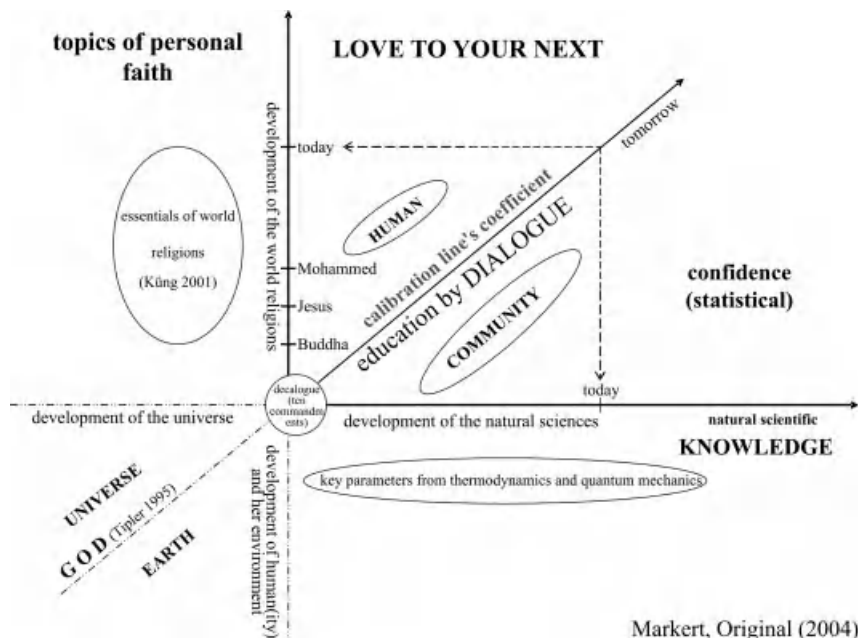


Figure 1.22 Creation of information as “*de novo synthesis*” produced by linking knowledge from natural sciences, belief in world religions (from Markert, Fränzle, and Hosang, 2005) and by use of a dialog education process (DEP).

developments in all global politics and technology make crucial decisions necessary to be fastly done on short terms. In a parallel development, international economics, people who are responsible in politics or society or all those taking part actively in life of society, that is, citizens in the originally French sense of the word, must restart looking for values and standards which hold generally in order to maintain society living in peace and security for the foreseeable future.

In this section we embark from the historical development of market-based economies, a common notion on the essentials and principles of democracy, to get an idea of the present situation taking into account the increasing social awareness of citizens in a civic society. Technological advances on information, communication and biotechnologies must be supplemented by smart, high-value decisions on competence in society.

For these ends, education must be considered as an integrative task based on becoming aware of changes in technology, and those in international and global common convictions and politics to get international support. An intelligent dealing with conflicts, supported by a democratic-minded majority, for integrative solutions of problems is crucial, where mutual trust counts more than the text of some treaty, where diversity of faiths and opinions are considered a tool for obtaining stability while solidarity toward the weaker in society must become more than a mere idea or aim (ethical consensus).

1.7.1

A Market-Based Economy

Man ever aims at getting more and the best. In a surrounding which is noticed as a possible threat, the weak appear to be objects for domination, competitors are seen as enemies and wealth just is a reward for the achievements in producing something. This human attitude, seen from now to present and bygone results, appears to be purely egoistic from a subjective point of view. However, exactly these egoistic features of character and thinking enabled humans to out-compete most other species during evolution in the past 80 000 years. Give and take, sell and buy, more generally speaking trading goods and services co-evolved along with cultural history of mankind, effectively cultural history could not be imagined to have occurred like it actually did without trade patterns.

Market-based economies generally depend on competition. At first glance, competition seems to cause hazards to individual existence since when one or two individuals (entrepreneurs) act on a common market and use it, this common use apparently mutually reduces their existence or at least performance (e.g., if their products are similar or they compete for the same group of customers). How well they perform and compete depends on their environment and living conditions, combined with specific bandwidths of tolerance and preferred conditions. Competition may change the notions of both tolerance (toward low wage levels, mediocre to poor living standards) and preference (high wage level, elevated living standards). Competition may occur on behalf of multiple primary and secondary mechanisms: factors among which the actors compete, such as customers, products, regions of marketing may be directly withdrawn, competition may be mutually inhibited by cartels or also dumping, or there may be modes of behavior pertinent to competition (threats, aggression, etc.).

Two quite similar entrepreneurs producing the same item for a limited system (market) will not coexist for long (independently). The reason is rather simple: it is most unlikely that the two entrepreneurs make exactly equally efficient use of some factor relevant in their competing, for example, of machines. Sooner or later one of them will perform better by their better use of the competition-pertinent factor. This entrepreneur is going to prevail, getting advantages from the ongoing competition. There is no reason to change or abolish this trend, and any system will just support a limited size of market simply for energetic reasons, hence the "worse" competitor is bound to vanish eventually.

However, almost every system contains entrepreneurs who are working on similar products and who (can) coexist. As a zeroth approximation the following rule holds: the more supreme (lacking behind) an enterprise is with respect to making use of its environment, the more (less, respectively) competition it may endure without getting removed by the competitors. Accordingly, the fewer similarities two enterprises display in their competition factors, the better and more easily the enterprises will coexist. Among very different economic niches, the chance will grow that competition to outside, toward other enterprises becomes less significant versus indoor competition.

To a nineteenth century entrepreneur, the worker/workforce was the most important factor in his enterprise. He was motivated by the longing to maximize private capital possession. This took people who would do the work in the enterprise; thus a historically novel part of society, the working class (blue collar workers) came into existence. The price (wage) to be paid for the work is given by “calculated work done per unit of time”. In all the ventures of the classical entrepreneur, value items are produced, which in turn create values in order to run a market economy. In markets, competition for customers is controlled and shaped just by supply and demand.

Later on, during the second half of twentieth century at least, it became obvious that exploiting nature by massively mining and using non-regenerative resources including hard to regenerate energy carriers [with this (ab-)use usually linked to an vigorously increasing environmental burden by pollutants which were released into the environment thereafter] was no longer accepted and tolerated by society. The phenomena observed then included the pollution of open waters, forest die-back, the Chernobyl reactor accident, the Antarctic ozone hole and possibly anthropogenic changes of global climate. Environmental problems thus arising and becoming evident were no longer an internal matter of the emitter countries because damage often arose also or even only beyond national borders. These transnational problems thus became international tasks also (Burtraw and Portney, 1991; Common and Perrings, 1992; Costanza *et al.*, 1997; Ellis, 1995, 2007; Fränzle *et al.*, 2005; Pearce and Turner, 1990). The Rio Convention of 1992 first had it that sustainability was to become the guideline to carefully deal with both nature and society on a global scales, with almost all countries being involved.

In several countries then legislation aiming to protect the environment was introduced and brought about serious criteria to be met by all branches of production and services (Elliot, 1995). However, generally speaking, these “green” developments of technology and legislation were only capable of tackling the so-called “external” pollution.

In this twenty-first century we are concerned with new kinds of problems which likewise call for novel ways of solving them (Beck, 1986; Biedenkopf, 1985, 1997; Markert, Fränzle, and Hosang, 2005; Miegel, 2005; Rosnay, 2000; Schellnhuber, 1998; Stern and Fineberg, 1996). Preconditions and tools to meet these tasks can be located “inside” humans, their psychosocial way of being, reflecting arguments and positions (which may, and often do, disagree) then to act in a manner which is distinguished by a high sense of responsibility for both oneself and others (Blackburn, 2001; Biser and Heinzmann, 2005; Choe, 2002; Ehrenfeld, 1993; Fromm, 1956; Hüther, 2003; Lapide, 1984; Norton, 1991; Rohrmann and Chen, 1999). Smart and non-violent management of conflicts—which is non-violent in both the material (no application of weapons) and the mental sense—will prove highly demanding both to the individuals and their views on public matters (De Young, 1993; Schwartz, 1994; Shrader-Frechette, 1988; Taylor, 1986).

Values like trust in some (economic) partner, a conscious promotion and protection of diversity, including different opinions in particular, and solidarity

toward those who “perform worse” in our society are values which will re-gain significance during this process (Farnworth *et al.*, 1981; Fischhoff *et al.*, 1982; Fisher, 1987; Gale and Cordray, 1994; Goulder and Kennedy, 1997; Hargrove, 1989; Meyer, 1997; Perrings *et al.*, 1995; Pickett, Ostfeld, and Shachak, 1997; Randall, 1988; Sachs, 2005). An intelligent handling of conflicts along principles given by trust, diversity and solidarity might prove key to developing an ethical consensus.

It becomes obvious that consensus apart from treaties depends and draws upon these values, rather than producing a contract or negotiating a compromise on some issue. In the future, the mere abilities of every single individual will shape motivation for living together in a society, rather than (over-)control by treaties, radical equality or social (over-)use (exploitation) of existing systems. These abilities refer to:

- 1) The ability to identify, define and honestly mention genuine conflicts and their reasons;
- 2) Act for a democratic yet speedy solution of problems based on free will and cooperation in a mind of partnership;
- 3) Do everything possible for man to realize solutions for corresponding problems jointly, sustainably and thoughtfully by all available means.

Modern results of psychology strongly suggest that individual “failure” in conflicts is an intrinsic problem in most cases and can be related to man having evolved from animals. “The strongest is going to prevail¹⁰⁴⁾” (by whatever means) is an idea that internally spoils individual thinking and habits of entire affluent societies, producing strong inclinations to make use of power, force and domination. How else can one understand that most individuals watch by media other people to starve (some 400 million children alone are below the level of “absolute poverty”, i.e., exposed to hunger!), and so do entire societies: this (non-)attitude can be considered a kind of terrorism (Gotzmann and Peschel, 2001; Henkel, 2002; Miegel, 2003; Sachs, 2005). This “inner pollution” of minds probably preceded and gave rise to the familiar “outer pollution”.

Among those challenges to twentyfirst-century humans, three must be mentioned which aggravate problems of global politics brought about and accompanied by fastly proceeding developments like those of informatics, communication technologies, molecular biology and genetic engineering. These challenges pose hazards for the further peaceful existence of the human race on this planet (Beauchamp and Childress, 1994; Markert, 2001; Osterwinter, 2002; Randall and Farmer, 1995; Schultz, Oskamp, and Mainieri, 1995). All three problems are capable of blowing up the web of society as we now know it; and more so if they interact they are really capable of destroying populations, which calls for an internationally negotiated settlement/agreement:

104) This is something quite different to Darwin’s principle of selective fitness “survival of the fittest” (in the given environmental situation and network of

demands and challenges) which obviously was both misused and deliberately distorted when transferred to principles of organization of human societies.

- 1) How to deal with the outcome of genetic engineering covering human reproduction also. Frankly speaking: what to do with those children born alive after “unsuccessful” genetic engineering and possibly considered a burden to society?
- 2) It is not yet settled how to get objective featuring of events in a multimedia-based word. Efficiency and mere speed of modern information and communication media can aggravate political miscalculations and wrong decisions if information is dealt with in an irresponsible manner (e.g., when reporting from war regions).
- 3) How to deal with convictions which are undemocratic, fundamentalist and often religiously underpinned? There are many examples from Israel, Ulster, the Basque areas, the United States and other parts of the world which suggest present democratic systems granting fundamental civic rights are (or were) incapable of meaningfully dealing with and opposing fundamentalists and other kinds of fanatics. The Kosovo intervention of 1999 was made by NATO—including German territory, airbases, pilots and equipment—without an UN mandate (thus avoiding a possible veto by Russia or China) in violation of international law!

History tells cruel lessons of what will happen if these problems combine and merge to bring about disastrous development, including genocide, propaganda, and fanaticism/fundamentalism.

1.7.2

Democracy and Its Limitations

Democracies deal with problems relevant to society by steadily balancing out the individual interests and common aims of society shaped by certain demands of acting in solidarity (Dahl, 1989; Dryzek, 1990; Pinzler, 2002; Rohrmann, 1994). Pursuit of individual interests must not restrain individual rights or even enhancing one’s own wealth, but likewise this clearly implies the duties of the individual to cooperate in a solidaristic community (Anscombe, 1958; Jonas, 1979; Kelly, 2006; Pearce, 1976; Rolston, 1994).

The state then is to provide and grant for some framework of laws and other rules that organize peaceful living together among citizens in a just, legal order. The state alone is allowed to use force (Figure 1.23). The rights and security of individuals are secured domestically by police and constitution-protecting services¹⁰⁵⁾ and many other institutions, while in international affairs the task of a state

105) Both authorities and judicial institutions in charge of protecting civic rights like the United States Supreme Court do. In the German original version of this text, *Verfassungsschutz* is mentioned (literally: Constitution Protection Agency) which refers to the German domestic secret service which is to observe and report on

(rather than curb!) extremist, antidemocratic or “counter-constitutional” political activities, be they left wing, right wing, islamist or run by sectarians such as Scientology. The *Verfassungsschutz* is entitled to take active measures only in terms of counter-terrorism.

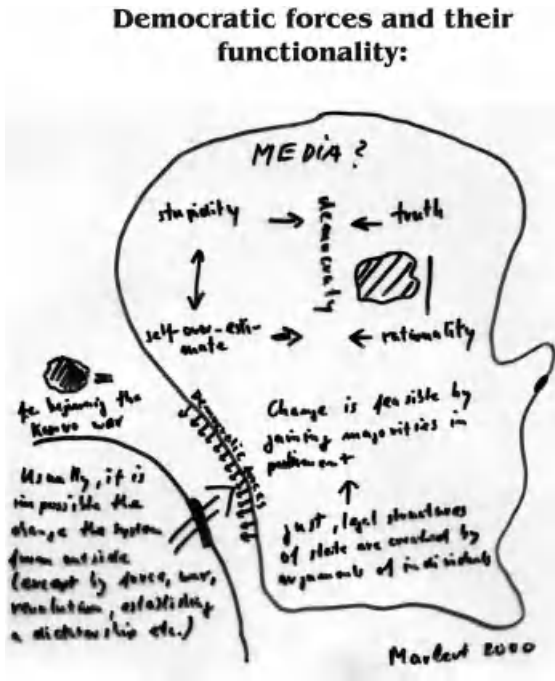


Figure 1.23 A simplified sketch of limits, boundaries set to a democratic system and its modes of functioning. The internal dynamics and stability of a democratic protocol of decisions release democratic forces and thus contribute to maintain rather stable limits of the system. Quality standards and smartness in parliamentary decisions grant for successfully dealing also with future, more complex and dynamic problem fields. The systems

requires stakeholders (politicians, entrepreneurs, parents, citizens) to steadily muse civil rights and duties of the individual and the solidaric society to adapt novel features to the system while avoiding biases, for example, in human rights terms and issues which would arise, for example, by deliberate violation of national or international law (Markert, 2003). More explanations are given in the text.

is to promote peaceful coexistence among forms of states which differ¹⁰⁶⁾ in both structures and aims. All states, societies and citizens then have their respective ranges of acting defined by the constitution. A system of law meant to balance individual interests and those of society gives a frame to oppose both individual offences (criminal acts) and extremist activities in society (e.g., those of left- or right-wing extremists).

106) However, in transnational structures like the Organization for Security and Cooperation in Europe (OSCE) or the Pan-American States Organization, some standards of democracy as well as peaceful procedures of settling domestic and international conflicts and achieving disarmament of the corresponding metaregions are

implemented even though not all OSCE member states actually conform to these principles. The European Council, for example, demands abolishment of death penalty by any state going to join and insists on the right to demonstrate for one's opinions, freedom of faith and the right to vote.

Further, the state support of peaceful coexistence within market-based economies must not limit individual freedom of shaping one's life too much, otherwise jeopardizing a "healthy" balance between individual and common interests. Free market economies simply rely upon individual initiative, his or her motivation and readiness to engage. If this readiness and corresponding individual responsibility is destroyed by excessive control of the individual activities by the state, markets (at least the legal ones) will break down. Such an excessive state control of individual activities and responsibility can also be caused by powerful administrative structures producing hierarchy and bureaucratic monsters which are capable of suppressing interests in private responsibility and economic activity.

Of course, specific kinds of religion can (and even must!) fulfill an important function in society, possibly producing even common senses of binds and duties in a society (De la Torre, 2004; Dürr *et al.*, 1997; Küng, 2001, 2005; Manzel, 2002; Markert *et al.*, 2006; Wabbel, 2004). Religions give incentives which provide an ethical orientation for an individual and entire (civic) societies. All over Europe, there are arguments from different notions of state and (vs roles of) society and of functions, roles of religious groups among "leftists" and "conservatives", "laicists" and those who promote a certain religion to play some role in society. These arguments are pertinent to the future role of Turkey in or beside an integrating Europe, likewise on the appropriate role and rights of orthodoxy: a "genuinely orthodox" shaping of relations between Church and state is an issue in all Greece and new European Union members Bulgaria, Romania, Latvia, Cyprus and so on. These differences in notions and concepts are borne out of different historical experiences also and become relevant if different ethnical groups meet, and they thus pose challenges to learning beyond borders. A kind of mutual trust in lieu of treaties will only be possible if this challenge is addressed. Notwithstanding this, a strict separation of church (religions) and state remains necessary.

Taking market-based economy and innovative power for granted and as the starting-point for improving understandings, concepts and structures of democracy, it still takes an arduous but probably successful way of optimizing systems soon for the generations to come. Here, methods of turbodemocratic¹⁰⁷⁾ implementation of urgent reforms and innovations are possibly useful.

1.7.3

Protocol for the Future: Grow along with Your Challenges

1.7.3.1 Thoughts on the Future

Often humans ask about the future: unemployment level predictions, stock exchange analysis, expectations on educational chances and outcomes, weather forecast for estimating whether one can have barbecue outside next weekend; these all require an educated guess of what is going to happen in the future.

107) "turbodemocratic" is a fast, high-quality process of decision-making during the identification and overcoming of problems, rather than the arduous, slow common approaches shaped by the wish of those involved to maintain their egos and powerbases.

However, “predictions are most difficult if they deal with future” (N. Bohr); this fact that the future cannot reliably be predicted, causing uncertainties and risks, is considered a dilemma because modern societies which cannot afford to improvise supply, which primitive ones would/could still do, require future development to be planned to some extent at least (Hill and Fowles, 1975; Markert, 2003). Hence, for example, population development (including demographic structure) and the spreading of diseases or epidemics must be predicted; and the use of non-regenerative energy carriers must be planned to obtain a responsible and sustainable society. On one hand, it is impossible to unambiguously predict future, on the other, we must do so to anticipate likely trends of development; this contradiction cannot be unraveled but we must practically accept it.

The principal reason why the future cannot be predicted is the high complexity of both functional and non-functional relationships in our environment, producing high dynamics, both endogenous and exogenous, in events and their changes. (Non-linear) changes in dynamics are best described by systems considerations using chaos theory, with deterministic chaos lurking in many features of developments most pertinent to our future. Of course, while the onset of chaos can be predicted, the state of a chaotic system after some period of unperturbed (or, worse, perturbed) development hardly can. Chaotic systems are most sensitive, amplifying the most minute changes in the starting conditions to large differences (Gotzmann and Peschel, 2001). To give an almost proverbial example, a butterfly putting a minimal turbulence to air when flying around at Hongkong might influence/“switch” the weather conditions in central Europe or northern America. Hence it is most difficult to obtain at least fairly reliable models which extrapolate spatiotemporal developments into the future covering the largest possible sets of starting parameters and their values.

Societies ever had to cope with future being uncertain; thus a glance into history might show which principal factors then shaped both technologies and society. The long waves of economy familiar under the term of Kondratieff cycles show that certain technological key advances are selected by global markets to “propel” the life of societies and global economies for quite a while (several decades). These crucial innovations include the steam engine, car and computer (Nefiodov, 1999). In highly developed countries,¹⁰⁸⁾ most citizens earned a significant improvement in their living conditions. Healthy food, high mobility, a large, diverse array of affordable items, but also communication and information and health sciences based on recent biotechnology are among the milestones that paved the way into some more qualitative and less sorrowful way of life.

Yet some two-thirds of mankind are still mainly excluded from this substantial improvement of life quality. Even worse, “affordable” workforce in so-called threshold countries [on the edge of thorough industrialization, like India, China (PR) and Brazil] is still used to maintain some difference in welfare, which is going

108) But it cannot be taken for granted that an already advanced economy will benefit from these periodical “pushes” to maintain a pole or at least comfortable position in global competition and development (cf. Argentina 1910–1950s).

to produce continuous decreases with respect to our common global political ends. The key area suffering from this is energy supply, with the remainder of affordable fossil energy resources going to be consumed during the next 50–100 years (in addition, releasing lots of CO₂). Furthermore there will be ongoing immense, and irreversible, losses of taxonomic species and of biodiversity, with annual destruction rates of primary rainforests being equivalent to the areas of about Switzerland or the Netherlands, without genuine substitution. Another urgent issue is to secure access to effective cures against epidemics like HIV/AIDS, which now are accessible for monetary reasons to only a small fraction of those most exposed, that is, in sub-Saharan Africa.¹⁰⁹⁾ People in “rich”, “healthy” economies could afford before, too.

With interconnections among different parts and structures of this world becoming ever more tense to end up in the globalization of technology, it is mandatory that all regions of this planet can take part in global markets as partners endowed with equal rights and chances. When there are political and economic instabilities in less privileged regions and states, this turmoil is going to destabilize the national economies of the wealthy North,¹¹⁰⁾ compromising our own standards of living.

Within industrialized countries, there are growing gaps between rich and poor also, with the chances/risks of social “rise” and “falldown” becoming more disproportionate than ever since industrialization. As a symptom of decreasing confidence in the future and its living perspectives, birth rates continue to fall, mis-shaping the demographic pyramid while trying individually to maintain an acceptable level of welfare.

Accordingly, gains in “organizing politics” which can be obtained from mere technological advances, with the aim of giving purely technological means to meet personal and inter-personal aims and longings, will serve by the way to maintain the present average level of life of an United States or Greek¹¹¹⁾ fellow-citizen, let alone further improve it.

Though translating economic interests into technological quality levels are indeed a lever to global economy, its actual positive political effects will touch only a small part of the world’s population. With the global population growing faster than exponentially (i.e., faster than ever before) while resources dwindle, counter-measures are most urgent.

1.7.3.2 International Quality Ends

While technological innovations are still needed, more success can be expected when trying to meet the life quality standards put forward by the World Health

109) Nowadays, there are programs in some of these countries, including South Africa, Botswana, and Uganda, to distribute antiretroviral agents, produced outside patent license coverage by exceptional agreements, for free to citizens who contracted HIV: one key reason for this is to avoid the breakdown of a qualified

local workforce rather than “mere” humanity.

110) Plus Australia, New Zealand.

111) This was written before onset of the 2008 financial crisis which hit Greece the hardest. But even before, living standards in Greece fell considerably short of most states in Central Europe.

Organization (WHO, 1996; Nefiodov, 1999). WHO states that almost all human beings, regardless of their places of living, cultural identities or other differences try to get:

- 1) Stable and positive self-estimate;
- 2) A positive attitude toward one's own body;
- 3) To be able for friendship and social relationships;
- 4) An intact environment;
- 5) A meaningful work done in healthy working conditions;
- 6) Knowledge about health issues and reliable access to medical support;
- 7) A livable present and a reasonable hope to have a livable future also.

Strangely, the roots of motivation of average German entrepreneurs to perform and live better in the framework of socially responsible market economy closely match the aims in living of every other man in the world, notwithstanding his/her occupation and site of living. Accordingly, we can hope that a means to improve conditions for everyone's quality of life should be found according to a common set of integrative approaches and measures, provided there is serious and honest interest in this.

1.7.3.3 Learn How to Learn

Hence it will no longer do in the future to use technocratic pieces of knowledge to obtain these integrative approaches to overcome the present problems, since:

- Increasing dynamics and complexities of problems need a better, more reflected arguing on pros and cons of some strategy;
- Crucial (or better: all future) decisions can (ought) be done exclusively based on provable, objectively stable pieces of information, data and knowledge, while:
- Sufficient transparency (in Russian: glasnost) must be provided to all the stakeholders.

With "performance being the personal ability of an individual to change and adapt", it takes "education providing the ability to be open and ready, able to learn on all levels".

Dealing with conflicts smartly and trying integrative problem solutions are more closely linked to each other than hitherto used to be assumed. Hence, life-long learning, achievement of quality and competences will get an ever larger relevance both to secure our common future in the society and for personal lives in the spheres of work and profession, family, leisure time, culture and politics likewise. The individual has to develop his ability to learn for this purpose and keep on learning as the way to obtain personal competence with regards to social, occupational and methodic acting (BMBF, 2001; German Federal Ministry of Education and Research). Concerning economy and society, these competences become crucial factors for innovation and capability of social self-structuring in order to compete successfully on an international level rather than losing contact to recent social and cultural developments.

We now need a broad movement to promote life-long learning both to develop and maintain individual living chances and to keep socially oriented democracy¹¹²⁾ fit for the future with regards to its economic, ecological, cultural and social perspectives of further development. The system of education must provide the basis to achieve this, given its ends, contents, structures and ways of acting and teaching (BMBF, 2001).

Life-long learning does not just mean to involve as many citizens as possible all over their life-phases (at least until retirement) but has qualitative drawbacks on education policy also. Life-long learning requires to change the attitude toward learning (BMBF, 2001), making learning a process the individual must pursue and shape all along lifetime responsible for him- or herself. With economic innovations and changes in society occurring ever faster, there is responsibility to autonomously adapt one's kinds of qualification. A new cultural sense is required which integrates learning into the processes of everyday life, acknowledging this and fairly estimates outcomes against the difficulties of this process (BMBF, 2001). Classical forms of learning and education offered by schools, professional training, university or secondary occupational education will not lose their significance but must be corroborated by a new key feature of informal learning, which takes place in the "school of life", in social networks, everyday life, at workbench, in family and leisure time. This is really a new principle of learning which must be developed, focused on one's own responsibility and capability to shape this process individually and autonomously (Dahrendorf, 1986, 2003; Goeudevert, 2000).

With a high degree of individual responsibility and autonomy being required, motivation and support of hitherto less advantaged groups must not be disregarded; these groups otherwise would not be capable of fulfilling such a task of self-motivation and structuring, as a rule. Education politics and practical education rather must be concerned and aware that nobody is taken off his educational and career chances. Groups who are now almost beyond the reach of education¹¹³⁾

112) In the German original: "*soziale Demokratie*". This term does refer/allude to "*soziale Marktwirtschaft*", the concept put forward by later Federal chancellor Ludwig Erhard (1897–1977), sometimes also dubbed "the Rhineland way of doing capitalism" rather than, for example, "*Archiv der sozialen Demokratie*" which is the central part of the party archives of the German Social Democratic Party (SPD). Anyway, in Germany the link between democracy/federal structuring of state and social norms is part of the constitution and even officially protected against any change (*Grundgesetz* articles 20, 79, 116).

113) In Germany this really became a popular term: "*bildungsferne Schichten*" (people

who live in utmost avoidance of education). The Programme for International Student Assessment (PISA) studies revealed Germany to be the one country in the developed world where educational and thereafter occupational chances depend most on the educational status (and income levels) of the parents, more so than even in many developing countries. So a vicious circle can be established (parental poverty precludes education of the children to a level now required even to obtain a reasonable apprenticeship position) which is avoided only by more active measures pointing to the corresponding milieu and urban neighborhoods.

must be integrated to avoid producing new obstacles in obtaining education and training. The present serious level and extent of exclusion of people and groups can be reduced in the near future only if the array of educational contents and kinds becomes more closely related to ongoing economic, cultural changes and those in society, while the offers must become more focused to the demands of any individual (BMBF, 2001).

With life-long learning becoming the paradigm of education, tasks and structures of classical agents of education must also adapt. A culture of learning which conforms to recent demands takes more and novel kinds of coaching and services, but also needs an enhanced degree of flexibility, self-responsibility and communication. These in turn require novel kinds of partnership with “consumers” and users of this broadened array of education. Institutions of education and culture, those concerned with social and youth welfare, clubs and enterprises, single persons and the activities of all of these must be pushed and motivated to investigate novel ways of learning by new kinds of cooperation (Hosang, Fränzle, and Markert, 2005; BMBF, 2001).

1.7.3.4 Transborder and International Regions of Education

Border transgressing regions of education which provide the chances of life-long learning working, and education to all childrens and youngsters but also parents, teachers and other adults, must be promoted better than before and get (placed) into the focus of public interest. Of course, diverging interests of political powers and parties, regional and national particular notions and interests will persist on either side of the border but there are also local commons which are a topic of (transcultural) education as such and itself can and must reshape present topic-focussed into ability-focussed curricula of education. A higher level of education becomes more attractive when people notice in remote border regions also: *tua res agitur*; it is your (local) matters that matter, rather than (just) the views and issues of some far away metropolitan region, far away in both topographical and mental terms. Besides better ways of overcoming local problems, this will enhance the wish and positive feelings on life-long learning, producing competences, self-confidence and thus finally increases occupational chances in border regions also. By the way, a kind of education defined and constructed like this is going to both catalyze and pay itself in the long term mainly.

There are plenty and more of historical burdens and present deviating interests; hence the first step must be constructing an integrative mode of conflict management on the very site which there gains support by some democratic majority. Rely on trust rather than treaty – this will work only if the above attitude is given. Diversities of opinions and religious faiths will only become a bonus and a chance to achieve more stability if we become aware of some ethical consensus which can be learnt and which is going to link us, including Muslim or agnostic fellow-citizens. This ethical consensus will include the tolerance of other positions and beliefs and likewise solidaristic acts toward the weaker.

1.7.3.5 Think Tanks Can Be Sites and Means of Smart Conflict Handling and Identify Integrative Solutions for Problems of Society

Problems and questions which recently arise in society are distinguished by multi-disciplinary and international ranges, hence highly specific expert knowledge and corresponding skills will not do to solve or even characterize and define such problems but it takes the readiness of everyone who is involved to mitigate among the often most diverse individual interests and wishes. Hence the crucial feature of an integrative problem solution rests not so much with technology or funding but with the actual “ability of everybody to honestly and convincingly achieve a solution which is acceptable to all the stake-holders”.

There are many features of conflicting double-binds in modern societies: politicians and the parties which “made” and support(?) them, officials including university professors in public service domains and authorities, physicians and their medical responsibility and ethos, TV producers and TV watching quotas, mothers and fathers who want both to perform and progress in occupation and responsibly, sincerely rise their children, they all are faced with conflicts which cannot be resolved and block potentials for overcoming these and yet other conflicts even though all are convinced that it takes genuine professional ethics, genuine convictions and their active realization in everyday life to ensure a sustainable and justly motivated structure of society!

In many different societies, psychological obstacles to adhere to these rules are posed by many citizens who already became solidly mistrusted and alienated by actions and premises put forward by politics itself. This alienation is but a symptom but it can block a real, honest dialog in society which is devoted to solving problems by innovative modes of thinking up to the point that it becomes impossible. Hence Miegel (2003, 2005) is quite correct in demanding citizens be fully and honestly informed about the situation before even starting a public discussion on how to deal with it, including the side-effects which would arise if the actual situation is neglected any longer. This will be the first rate of a “pound (weight) of honesty”: politicians and others in charge of decisions pertinent to society must be courageous enough to be (recklessly and fully) honest. Viable data on the situation and complete transparency toward all ones who are or could become involved are self-evident conditions to get any reasonable acting which can make a meaningful future.

1.7.3.6 How Much Time Is Left for Solutions Taking Care of and Integrating the Present Problems?

Realistic estimates of the time left to mankind to tackle problems in an integrative manner on global scales, implement and complete them range from 500 to 1000 years from now. Table 1.6 gives the necessary or possibly optional conditions and steps for this kind of global change. Maybe by 3000 there will be some merger between human and nature shaped like a symbiosis (Rosnay, 2000). This would be a harmonized balancing of all the inputs and outputs among all the existing biocoenoses for common and mutual benefit which to plan and realize must be the priority and aim of all human activities then. To achieve this end, it will take

Table 1.6 Global trends of development predicted for this new, just beginning millenium.

By 3000: Man joins a symbiotic relationship with society and the ecosystems in order to survive. He is going to become a symbiotic cell of a huge planetary organism starting to live based on itself: a macroorganism on which our future depends (Joel de Rosnay, director of the museum of future technologies at Paris; Rosnay, 2000).

By 2500: A just world can only be created if the last dictatorship has been abolished providing the key condition for global justice which is peace. This is going to happen 500 years from now (Goeudevert, 2000).

By 2100: Assuming a further exponential development/increase of our mental capacities for a conflict management which becomes most urgent in the future, the recognition that a more just future world cannot be achieved without global peace will set foot all around the world.

By 2030: Creation of the precondition (by 2022–2028) to abolish the present state of “hunger terrorism” which hits large parts of Africa and to put an end to it by the end of this century (“turbodemocracy,” Markert, Fränzle, and Hosang, 2005).

1000 years of global education, which must of course be developed, discussed and effectively implemented for gaining acceptance among all mankind. The practical result which is inevitable is to agree on a globally common criterion of completely just distribution of material and non-material goods and items among all people living on Earth. Before this can be reached, constant global peace must be achieved, which will be about 500 years in the future. In addition, this will be the period of time until the downfall of the last dictatorship on Earth. This is another precondition for the era of stable global peace predicted by a number of colleagues, which in turn is indispensable for justice in the above sense, namely the just and balanced distribution of all the essential goods.

Table 1.6 gives an idea of the timescale it might take to implement the necessary changes in a “turbodemocracy” once there is common acceptance of education being most urgent: until 2030. This is the period of time it will take to harmonize and equalize in rank intercultural and intracultural activities regarding the many diverse spheres of interest—national and international, mono- and multidisciplinary, regional and transregional. There is a desire to give, to share, to understand and to accept other people and cultures which is corroborated by enlightened self-interest, acknowledging that this is the only feasible way to possibly and satisfactorily ensure one’s own existence, and this promotion by enlightened self-interest will make us “donate” education and professional training to entire parts of continents such as Black Africa within one generation’s time, about 30 years from now. To realize and implement this will become a common task giving the chance to live in about the decent and self-determined way of decisions after all which we are completely accustomed to. The latter global process may be completed by 2100.

1.7.3.7 Conclusion

Questions and demands of future will not depend so much on the way to decide whether a new street is planned for purely economic reasons or canceled to protect the environment but how fast and efficiently a decision can be done which satisfies all the involved by some consensus. The “mental blockers” mentioned above are often going to block rational and reasonable solutions, removing the chances of gremia and councils to decide and act successful and efficiently; thus think tanks which are focused on jointly finding problem solutions are most urgent to establish (Pinzler, 2002). Think tanks are established in United States political counseling for as long as project teams last and they cooperate for several months. These teams are completely independent of political parties, industrial and other lobby groups and are distinguished by utmost competence on their issues; thus they can develop and offer stake-holders some recommendation how (on which way) to solve their specific problem.

Think tanks can be associated with schools, universities or other sites of (occupational) education where people meet, live, develop, negotiate and face arguments. Likewise think tanks can be private institutions (other than private universities) where specialists trained in interdisciplinary thinking create both fast and realistic solution approaches. This can shorten that almost infinitely long, bureaucratic and unbearable route from identifying the original problem to the supreme decision maker and serve to relocate the solution next to its topic. Creative potentials of those taking part are considerably enhanced, increasing readiness to find solutions by personal considerations, experiences and understanding. Think tanks are not primarily challenged with time shortages, while honestly telling that a problem cannot be solved by now because of lacking capacities and pieces of information would suffice to avoid decisions which are premature or outgrowths of political bias. Regional think tanks can thus be a valuable and important tool to develop new strategies, ideas and finally innovations.

This means education and professional education will decide about life chances in the foreseeable future (Figure 1.24).

Everybody needs education! Once this is generally acknowledged (hopefully soon), there also will be substantial funding for all respects of education. Parents, children, pupils, students, teachers, people in occupation and retired ones will see and be able to attend informal colleges,¹¹⁴⁾ kindergartens, integrating centers where youngsters, elderly and other people meet, elementary, occupational and highschoools where both teaching and learning are fun again, aiming to be a little better than your neighbor while sharing joy with learnt matters can also go without saying once again. “Knowledge must turn into love” (Choe, 2002). Smart management of conflicts and integrative ways of dealing with problems thus are very

114) In original German: *Volkshochschule*. These are public institutions which have their part in advanced (not apprentice) professional education, besides universities and universities of applied sciences. There are also courses in

computer skills or various modern languages. Some certification of courses at *Volkshochschule* can actually be used in a profession, unlike a university; an Abitur (school leaving examination) is not required to attend.

Ethical Consensus

trust is better than negotiating treaties,
diversity is a condition for stability, and
the weaker deserve and can rely upon *solidarity*.

a smart method of conflict management which provide integrative solutions of problems.

Regions concerned with education → learn how to learn
+ ↓
think tanks → to define integrative solutions for problems
+ ↓
turbodemocracy → to get faster results

(Markert 2002)

honest approaches. We shall describe some of these in the forthcoming chapters of this volume. Yet honesty takes its price, a price which cannot yet be figured in £, € or \$ exactly. But would you like to get some more of it?

By now, we can still freely decide which way to go. We consider that one outlined above to be a peaceful one which cares for human dignity of individuals next to you allowing it to be taken and accepted and succeed. We must be aware there are lots of “scrub” along this—and every other path—which must not be trampled down or destroyed without a chance to retrieve or recover it. Nature, on its part, most often, perhaps all too often, shows that it is going to accept and nourish us. In a partnership, we ought to offer a fair compensation.

Of course, there are alternatives at hand which appear less arduous at first glance. Other, “easy” ways are seductive, displaying, loud, colorful multimedia coverages. It is fun to make use of this while not caring for tomorrow. However, the outcome of this way has been war among peoples, at least 11 000 times just in the 2000 years since Christ was born.

2

The Compartments of the Environment – Structure, Function and Chemistry

2.1

The Three Environmental Compartments and Their Mutual Interactions: Lessons for Environmental Situation Analysis and Technologies to be Learned from Comparative Planetology

The three environmental compartments differ considerably with respect to their properties, for example, concerning density (by >3 powers of ten), mobility and capacity to absorb, dissolve/spread and transport pollutants. Moreover, certain kinds of physicochemical interaction and chemically effective energy propagation are either permitted or blocked by the principal features of these compartments, for example:

- There is no photochemistry in soil.
- Sonochemical reactions require neat liquids or at least fully soaked sludges.
- Mechanochemistry happens only with solids subjected to the milling/break-down of individual crystals.
- There is no adsorption to gases (rather than to liquid or solid interfaces), hence, no heterogeneous catalysis can occur in an atmosphere, except for aerosol formation [the formation of NH_4 salts in both Earth and Jovian atmospheres (acid = H_2SO_4 , HNO_3 on Earth, H_2S , HCl on Jupiter), water ice, photochemical aerosol formation from organics (via C_2H_4 , C_2H_2 , HCN ; Jupiter, Titan, possibly early Earth)] or “mechanical” input (meteorites, volcanoes).
- Biogenic materials, for example, enzymes liberated from dying or mechanically destroyed cells, can operate as catalysts or at least sorbents for quite a while thereafter (even if they are no exoenzymes) in either soil or water.

In addition, interactions can bind, mobilize (erosion) and otherwise influence the fates of environmental chemicals and the possible exploitation of energy sources [e.g., coordination photochemistry of Fe(III) and other complexes, photoelectrochemical turnovers on Ti-containing or ferric phases]. Thus it is worthwhile to compare Earth – possibly separated for various climatic and ecological regions – to

the other planets, dwarf planets¹⁾ and large moons accompanying her in “our” solar system²⁾. On Earth, we are most accustomed to the interactions among the three environmental compartments air, water and soil to shape both surface features and control chemistry of the planet. Fluvial erosion, the structures of forests and pedogenesis by biota are but examples of this. Quite a few other bodies in the solar system have been discussed to bear life before now, or have done so in early stages of planetary geochemical and fluid system evolution, including the atmospheric droplets of Jupiter and the sub-surface regions of Mars and the satellites Europa, Enceladus and Titan. Even if life actually made its way there protected from UV and ionizing radiation (radiation belts) and barren cold or (except for Titan) lacking sufficient atmospheric pressure to sustain surface liquids, it is yet safe to maintain that nowhere else in the Solar System did or do biochemistry and biogeochemistry interfere to any relevant extent with the interactions between the environmental compartments—if all three (still) exist there. So let us address the latter question, including phenomena from gas–condensate interactions which will additionally influence chemical transformation in or below the atmosphere, namely cloud formation and—derived from this—the possible occurrence of lightning bolts and thunderstorms which can be detected in outer space by their radio signals (quite familiar to those who still obtain radio transmission by an aerial). Clouds are possible sites of gas–liquid chemistry (sometimes in highly acidic media) and exclude most of photochemically active electromagnetic radiation from passing to lower levels and the surfaces whereas lightning bolts combine spark-discharge and shock-wave induced chemistry to enable transformations which even activate N_2 to introduce N into reactive species such as N_2O , NO (Earth) or HCN, HC_2CN (Titan, Jovian planets), considerably enhancing N turnover rates even though energy throughputs are rather limited. As both lightning and clouds in general imply some gas–liquid interactions, lightning requiring turbulence in addition, the very occurrence of these phenomena spells the coexistence and interaction of two environmental compartments, regardless of the respective compositions of liquids and gases [e.g., 85% sulfuric acid and molten sulfur (two cloud layers) vs CO_2 + traces (SO_2 , COS, HCl, CO, N_2 , O_2) on Venus] which are com-

1) A category recently introduced to describe objects sufficiently large to become almost spherical by force of their own gravity but too small for their gravitational perturbations to “sweep clean” the surrounding of their solar orbits. The largest ones so far known are Eris and Pluto with some 2300 km diameter each (Matson, 2011), both accompanied by moons. Atmospheres do exist near perihelion in either case but it is neither known nor likely that liquids (e.g., dinitrogen, CO) will persist under the tenuous atmospheres at the surface. However, such liquids might roam, dissolve organics and inorganics and be occasionally ejected into the atmosphere

just below the surface much as is observed on Saturnian satellite Enceladus (much smaller than the dwarf planets though spherical) or on Triton (which, to our present knowledge of the latter ones, is very much comparable to Pluto and Eris though a little larger).

2) Although >500 exoplanets are known now, for dozens of which spectroscopy may be feasible upon transit in front of their central stars, there are very few instances for which actual data are available. In addition, these are very large “gas planets” which presumably do not have any large consecutive liquid volumes (beyond the size of cloud droplets or possibly raindrops), let alone lakes or oceans.

pleted by the solid support in either terrestrial planets, large dwarf planets and planet-sized moons to permit full triple interactions.

It is so essential to life—and also it reflects the living conditions our Pleistocene ancestors looked up by intuition—to have these interactions among all three environmental compartments and the biota to an enhanced level that the ancient cultural concept of *locus amoenus* (pleasant site) inevitably already contained this [for more recent variations of this probably archetypical concept(-ion), either consider Gauguin's Tahiti paintings or just flick through a vacation catalog]. This is why the triple interaction is explicitly addressed in Table 2.1 while even very large volumes of liquid may persist indefinitely beneath some ice cover even if there is no substantial atmosphere (on Mars, centimeters to decimeters of regolith will do), like on Europa and Enceladus.

A “real”, sustained atmosphere (not subject to substantial steady losses into outer space like with comets) takes sufficient gravity attraction to the gases, that is, the planet or moon must be sufficiently large and dense and there must be no excessive heating of the upper layers³⁾. If the atmosphere is dense enough to be (essentially) retained over large periods of time⁴⁾ and possibly stabilize some component of it as a liquid on the surface (gas planets to be excluded from this consideration as they possess an extensive atmosphere, but no real surface, *by definition*) the maximum speeds of gas particles should be about one-sixth of the escape speed at most. Hence the corresponding discussion restricts itself to the four terrestrial planets, the two biggest dwarf planets, the four gas giants and eventually seven moons of Earth, Jupiter, Saturn and Neptune the diameters of which (between 2700 and 5300 km) compare well with dwarf planets (Triton probably even was one in earlier days) or smaller terrestrial planets. As for smaller moons

- 3) An excessive heating of upper layers and loss of (in particular) hydrogen (vs deuterium, the same with heavier elements) can occur by each of several mechanisms:
 - 1) Photo- or radio- (cosmic radiation) chemical formation of radical or atomic, molecular ions which then react with water vapor or other “hydrides” to yield energetic, high-speed H atoms or protons which readily leave the upper atmosphere against gravity if the free wavelength exceeds a few kilometers (in sea level air at about 1 bar it is 80 nm, for comparison).
 - 2) Accumulation of argon which conserves radiation energy in long-lived excited states (much like helium and neon and krypton, used therefore in lasers, also do) which are de-excited by collision, passing the energy into acceleration or molecular splitting of the collision partners. Thus, a thermosphere can be heated to some 10 000 K by just a few percent of argon, like in Earth and Martian atmospheres. CO can effect the same by populating a carbenoid triplet state in atmospheres of all Mars, Titan and Pluto, causing similar energy storage before chemical cleavage by insertion into CH or OH bonds, producing aldehydes, formic acid or its esters.
 - 3) The “classical” greenhouse effect; IR-absorbing species like CH₄ are also present in Earth's lower ionosphere.
 - 4) Something like 10⁷ to several 10⁸ years; concerning longer periods of time, Martian atmosphere—and possibly those of certain moons—had been much denser than now, Venus lost lots of water and even Earth had so much denser an atmosphere just 350 My ago (in the Devonian) that huge dragonflies (*Meganeura*) could get and keep airborne, with subsequent pressure decrease accompanied to a mass extinction (Permo-Carbonian ice age).

Table 2.1 Celestial systems inside the solar system and environmental compartments existing there, including chemical remarks.

Name, kind	Diameter at equator (km)	Central body	Atmosphere, composition [P_{surface} (bar)] ^(a)	Clouds, composition	Lightning discharge	Soil, chemical composition	Fluid basins, chemical composition
Terrestrial planets							
Mercury	4878	Sun	None ($\approx 10^{-15}$)	None	None	Silicates	None
Venus	12100		92; CO ₂ + N ₂	Yes, sulfuric acid (upper) and liquid S (lower)	Yes	Volcanic origin, resembling basalt	Locally molten salts (?)
Earth	12756		1.01; N ₂ + O ₂ + Ar + H ₂ O	Yes, water (ice)	Yes	Sediments partially biogenic, partially volcanic material	Water containing dissolved salts (NaCl and others)
Mars	6770		0.006; CO ₂ + N ₂ + Ar	Morning fog, cirri, sometimes snowfall	No	Regolith, Eolian and aquatic sediments, aquogenic salt layers (e.g., epsomite, jarosite)	Salt lakes and possibly oceans (H ₂ O) in earliest times
Gas planets							
Jupiter	142700	Sun	H ₂ + He	Several cloud layers, including NH ₄ salts, NH ₃ and water	Yes	No	No
Saturn	120800 (rather oblique)		H ₂ + He	yes	Yes	No	No

Uranus			$H_2 + He, CH_4$	No	No
Neptune	49066 (1 bar level)		$H_2 + He + CH_4 + N_2$ (the latter inferred from HCN abundance)	Yes	No
Dwarf planets		Sun			
Pluto	2300		About 10^{-6} ; $N_2 + CO + CH_4$	Yes	?
Eris	Some 2300		Strongly dependent on phase of sun orbit, now $<10^{-9}$		?
Ceres	950		None	Water ice, organic admixtures	None
Satellites					
Moon	3476	Earth	None ($<10^{-13}$)	Silicate and phosphate (KREEP ^d) regoliths	None
Io	3638	Jupiter	$0.3 - 3 \times 10^{-9}$; SO_2		
Europa	3070	Jupiter	10^{-12} ; O_2	Solid water ice, SO_2 , frozen H_2SO_4 , O_2	Large water basins under a few km of ice
Ganymede	5262	Jupiter	$\leq 10^{-11}$; O_2		Salty ^e water under some 200 km of ice

(Continued)

Table 2.1 (Continued)

Name, kind	Diameter at equator (km)	Central body	Atmosphere, composition [P_{surface} (bar)] ^{a)}	Clouds, composition	Lightning discharge	Soil, chemical composition	Fluid basins, chemical composition
Callisto	4820	Jupiter	7×10^{-12} ; CO_2			Silicates, water ice, solid CO_2 , SO_2 , NH_3 , organics	
Titan	5150	Saturn	1.5 ; $\text{N}_2 + \text{CH}_4 + \text{Ar}$			Water ice, many organic compounds	Large lakes (polar regions), rivers, probably containing liquid CH_4 ^{b)}
Rhea	1600	Saturn	10^{-12} ; $\text{O}_2 + \text{CO}_2$				None
Triton	2710	Neptune	$2 - 6 \times 10^{-5}$; N_2 , traces of CH_4 , no CO			Water ice	

- a) For gas planets it is impossible to give a surface pressure as there simply is no gas/solid interface corresponding to upper soil layers. However, gases get almost incompressible (quite similar to liquids and solids) at several kilobars, and even lower inside Jupiter and Saturn highly compressed plasmas get steadily converted into metallic states at $>10^5$ bar ($>10^{10}$ Pa) and temperatures of many 10^3 K, whereas for both Uranus and Neptune the much larger shares of CH_4 in their atmospheres will then decompose into the elements – H_2 and diamond (f). For chemical purposes, the lower edge of the convective regions (determined from upwelling of non-equilibrium species formed in a hot environment, like PH_3 , CO , GeH_4 , AsH_3 or HCP) can be taken as the lower end of the corresponding gas planet's atmosphere: for Jupiter 1000 K, >300 bar; Saturn about 800 K, 400 bar; Neptune T undetermined, P probably in excess of 1000 bar; Uranian atmosphere is hardly convective.
- b) The extent of fluvial erosion suggests polar admixtures such as methanol CH_3OH or acetic acid to contribute to dissolution of water ice surfaces.
- c) Convection of salty (thus, conductive) water beneath the ice shroud causes Ganymede to be the only satellite with a magnetic field of its own.
- d) KREEP means K, rare earth elements, phosphate.

of whatever planet, the next ones, Rhea, Iapetus (both orbiting Saturn), Titania and Oberon (orbiting Uranus) at some 1500 km or Charon (orbiting dwarf planet Pluto), Thetis and Dione (moons of Saturn) are so much smaller (at least a factor of 20 in mass) that they would be considered to belong to another category than the seven ones mentioned before even if one or another would display some tenuous atmosphere due to venting (like Enceladus does), and the same holds for other dwarf planets like Ceres or Sedna. Hence Table 2.1 is restricted to 17 objects (+ Ceres), with too little being known about exoplanets (planets orbiting stars other than Sun, some 500 being known now) to make any corresponding statements. Thunderstorms are to be taken as an indication of intensive atmospheric (gas/liquid) or suprasurficial (gas/dust from aerial erosion) interphase interactions eventually causing electric charge separation and thus an argument that “relevant” interactions occur beyond macroscopic morphological erosion patterns. To sum things up, there is or was complex, full-scale triple interaction among environmental compartments on Earth, Triton, Titan and Mars, maybe Venus.

Concerning atmospheric components, only the two most abundant ones are listed except there are third ones comprising about 1% (H_2O on Earth, Ar on Earth, Mars and Titan, CO on Pluto) or more.

The full-scale interaction among environmental compartments so familiar on Earth thus depends on an appropriate planet size: if it is too large, there will be a vast gas cover around a small core, if it is too small, it may yet be geologically active, including venting volcanoes and geysers, for quite some period of time but under a [then very tenuous (10^{-12} – 10^{-5} bar)] atmosphere oceans will only persist if covered by lots of ice, precluding any quantitatively significant exchanges of matter or energy among the environmental compartments (except, possibly, for “sea-floor”). This, for example, holds for Ganymed. The “meaningful” range will cover solid celestial bodies ($P_{\text{surface}} < 100$ bar) with diameters of some 3000–13000 km. On both Titan and Earth, there are full-scale meteorological cycles of compounds which comprise several percent of the atmosphere (CH_4 ⁵) and H_2O , respectively). Sharp-edged craters like in Figure 2.1 are typical of such celestial bodies which both an atmosphere and a liquidosphere and thus see minimal erosion on the surface. Here, “soil” is the only environmental compartment. If there is interaction (Venus, Earth, Mars, Titan), however, then the craters have “smooth” edges due to erosion.

Another peculiarity common to Earth, Titan, Triton (and perhaps some other very large Kuiper-belt objects) is that the liquid which connects atmosphere, liquidosphere, and surficial erosion is a main component (some 3% with both Earth and Titan, almost 100% on Triton) of some atmosphere dense enough to have “weather activities” but not too dense to have light penetrate it or to cause extreme greenhouse heating. Although neither liquid nitrogen nor methane, ethane do dissolve water ice or salts, there is pronounced fluvial and shoreside erosion on Titan. Apparently water ice and hydrocarbons known to exist in the soil surface

- 5) The surface of Titan strongly resembles that of Mars on a small scale, including sky color (orange). Fluvial erosion takes place by a liquid mixture which contains CH_4 , N_2 , C_2H_6 and others, possibly to be enhanced by solvation interactions.



Figure 2.1 The four terrestrial planets and typical landscapes encountered thereon in comparison. From top down: Mercury, Venus, Earth and Mars (cf. Table 2.1). © 1997 Calvin J. Hamilton.

(acetylene, propyne, benzene, etc.) are partly dissolved by hydrocarbon rainfall, partly ground down mechanically and dissolved by possible photogenic admixtures such as methanol CH_3OH or acetic acid. Thus Titan's rivers and lakes produce substantial surface erosion, with geysers venting corresponding on other (smaller) celestial bodies with or without prior dissolution (Triton, Saturnian satellite Enceladus).

2.2

Properties of Earth's Environmental Compartments and Resulting Options to Clean Them

We shall begin this consideration by introducing the idea of environmental compartments acting as reactors⁶⁾ even before discussing them one by one; although the idea of reactor might appear trivial given the plethora of chemical reactions taking place in the compartments or considering corrosion or inside your own breath, the reactor concept means putting the focus on it. That is, neither in transferring the reactor paradigm to environment nor in technical chemistry or fission technology can a reactor be taken as a passive volume, rather it both spatially organizes the ongoing processes and directs or influences them by both selective catalysis (platinum group metals in three-way exhaust converters) and inhibition (control rods of a nuclear fission reactor). Like in technical chemistry, processes in environmental compartments other than soil are influenced by photochemical energy inputs, generally permitting to compare the local processes to those in technical devices. As environmental engineering is just about interfering with such natural or para-natural (spontaneous processing of components themselves introduced by man) processes, both description and operative action will be based on corresponding comparisons. These are heuristically most valuable therefore.

2.2.1

Atmosphere

The atmosphere is a complicated mixture of mainly gaseous compounds and elements of all abundant and rare, highly (free radicals, element alkyls) to non-reactive (noble gases, N_2 , element perfluorides like CF_4 , SF_6) components (Table 2.2). After being formed by human input, bio- or photochemical reactions,

6) The idea to think about soil as a kind of chemical reactor and pedogenesis being both site and product of these transformations can be traced back to the father of pedology (soil science), Vasily V. Dokuchaev (1846–1903). It is due to his ideas shaping pedology that there are many kinds of soil now globally named with Russian terms, like chernozem or podsol. Later, Berkeley-based Swiss Hans Jenny

(1899–1992) put the pedological reactor concept into quantitative terms, also by radiolabelling experiments on soils and roots (Jenny 1941; Jenny *et al.* 1939, 1950). In limnology and ocean sciences, concepts like that of residence time of some solute or reactive species are likewise borrowed from chemical reactor attitudes of view (Sigg and Stumm 1996).

Table 2.2 Composition of terrestrial atmosphere (after Lewis and Prinn, 1984, with additions).

Gas	Share (ppm)	Origin	Lifetime (years)
N ₂	781 000	Volcanoes, denitrification	16*10 ⁶
O ₂	209 500	Biogenic (photosynthesis)	3000
Ar	9400	Traces are primordial (^{36,38} Ar) ^{a)} , most (99.6%) from radioactive decay	Permanent (noble gas)
H ₂ O	<40 000	Volcanoes, cometary impacts	0.025 (atmospheric lifetime till rainout, hardly chemical transformation)
CO ₂	370	Volcanoes, both bio- and anthropogenic	Ca. 100
Ne	18.2	Primordial	Losses by effusion to space?
He	5.24	Radioactive decay of α -emitters	Ca. 10 ⁶ (losses to outer space)
CH ₄	1.8	Biogenic, agriculture	4–5
Kr	1.14	Primordial	Permanent (noble gas)
H ₂	0.4–1.0	Biogenic, and photolysis of HCHO and H ₂ O	2–3
N ₂ O	0.3	Biogenic, agriculture	170
CO	0.01–0.2	Volcanoes, combustion	0.4
Xe	0.087	Primordial + radioactive decay of ¹²⁹ I	Permanent (noble gas)
O ₃	<0.05	NO ₂ -based photochemical processes	5*10 ⁻⁶ (a few minutes)
NH ₃	<0.02	Biogenic	0.01–0.03
SO ₂	<0.02	Combustion, volcanoes	0.01
H ₂ S	0.002–0.02	Biogenic, volcanoes, hot springs	≤0.1 (typically 0.008)
HCHO	<0.01	Methane oxidation	0.0005 (daytime, due to rapid photolysis)
SF ₆	0.0036	Anthropogenic (used in electric switches)	3200
•NO ₂	0.003	Combustion, and biogenic (nitrate reduction)	0.1
•NO	0.003	Like •NO ₂	Ca. 0.001
HCl	0.0015	Volcanoes, combustion	Ca. 0.01

Table 2.2 (Continued)

Gas	Share (ppm)	Origin	Lifetime (years)
HNO ₃	0.001	N oxides + air/water; •NO ₃ + R-H	Ca. 0.02
H ₂ O ₂	0.001	Water photolysis	
CH ₃ CN	0.0008	Forest fires, unidentified additional sources	Ca. 20
C ₆ H ₆	0.00075	Combustion, forest fires, volcanoes, landfill gas	0.025
CH ₃ Cl	0.0006	Marine algae, volcanoes	1.5
COS	0.0005	Photolysis of aquatic S-organics in ocean	>50
HCN	0.0001–0.0009	Combustion, pyrolysis of N-organics	Ca. 0.2
CF ₂ Cl ₂	0.00028 in (1982)	Anthropogenic	Ca. 150
CCl ₄	0.00012	Solvent (discontinued), marine algae	50–70
CHClF ₂	0.00011	Anthropogenic	12
(CH ₃) ₂ S	0.0001–0.00015	Marine algae	0.0015
H ₂ SO ₄	0.0001	SO ₂ oxidation	0.02 (leaching)
CF ₄	0.00007	Aluminum smelters	50 000 (!)

- a) With noble gases (Ne, Ar, Kr, Xe) primordial means being there in its present chemical speciation form (i.e., atomic) ever since the Solar System was formed and then introduced into planetary materials. After inclusion, venting to the atmosphere took place by volcanoes or other kinds of melting the original matrix containing them. Radioactive decay is given as a source only with those nuclides long-lived enough to have undergone inclusion into planets (rather than into chondrites only) only then and there to produce Ar or Xe by decay (⁴⁰K, ¹²⁹I and nuclides capable of spontaneous fission like ²³⁸U, ²⁴⁴Pu). Apart from noble gases, such secondary release is impossible since all other gases, including N₂, are way too reactive.

There are other strongly toxic, oxidizing or/and irritating gases and vapors besides of HCN in the atmosphere, including formaldehyde HCHO, CO, benzene, HOCl or NO₂. Although the presence of and UV absorption by ozone in the stratosphere is most important for us, it is simply a toxic and aggressive nuisance next to Earth's surface in the troposphere.

combustions (from wildfires to engines), these are capable of reacting with one another, dissolve in water or otherwise interact with it or/and with soil, biota. Hence air, displaying a well-differentiated structure, interacts with all other environmental compartments. Vertical transport is far slower than the horizontal one; there is unmixing in favor of light gases hydrogen and helium⁷⁾ in large altitudes.

- 7) Though there still is sufficient N, O, N₂, O₂, and Ar and corresponding radical cations to produce intense emissions in aurorae even at >400 km, H, H₂ and He do prevail.

Both concerning general properties and risks air is exposed to partly result from this structure and from differences in reactivity: poorly reactive species (say, $\tau_{\text{troposphere}} > 0.5$ year) can be transported to remote sites, getting into more activating conditions (UV wavelengths, etc.) and cause damage there (e.g., CFCs).

You will be familiar with the dominant components of the atmosphere (plus some often-discussed trace gases like noble gases, CH_4 , N_2O) but in fact there are dozens of additional compounds down to the 0.1 ppbv⁸⁾ (100 pptv⁹⁾) concentration level, plus dozens more from that down to the determination limit (now, ≤ 1 pptv), even disregarding main and trace components of aerosols.

Nowadays, even gases which are considerably more dilute than perfluoromethane (CF_4 ; 70 ppt), the last entry in our above list, can be identified and quantified precisely, down to about 1 pptv or somewhat less. However, most of these are so rare because they are highly reactive (rather than containing “exotic elements” like Se, As, metals), with only the free radicals at such levels [OH , at some (average) 20–30 ppq (parts per quadrillion, 1 in 10^{15} , or 5–8 times 10^5 molecules/ cm^3) or OBr at some 100 ppq] being considerably involved in chemical cycles. At a few ppb, sulfur compounds SO_2 , COS , H_2S and H_2SO_4 dominate and construct the cycle of a principal bioelement in the atmosphere, as do chlorine compounds HCl , CH_3Cl at somewhat lower levels (a few hundred ppt). Frankly speaking, the list was somewhat arbitrarily terminated at some 10^{-10} times the concentration of N_2 as dominant atmospheric component (i.e., at 78 ppt), with some “interesting” compounds (dimethylsulfide, H_2SO_4 , CF_4) having about this abundance.

Atmospheric gases are subject to both adsorption and chemical reactions, both possibly influenced by simultaneous impacts of light and UV radiation. As adsorption is an exothermic process and reactions with soil particles may be also, the stability of air components like CO_2 or O_2 or halogen compounds (e.g., HCl) sensitively depends on both temperature and soil liquid pH. In turn, effects of these compounds in the atmosphere—from greenhouse activity to interaction with biota, be the latter a support or nuisance to life—will be controlled by the same factors. On Venus ($T \approx 740$ K), a really devastating greenhouse effect is maintained by the lower atmosphere being too hot to allow substantial CO_2 cleavage by silicate or oxide rocks even at 9 MPa partial pressure of CO_2 while on Mars (T about 220 K, with large annual and diurnal variations) Fe oxides of both valence states (Martian regolith is ferromagnetic in parts which means maghemite $\text{Fe}_2\text{O}_{3-\delta}$ or even Fe_3O_4 must be there; Hennig and Rehorek, 1987) and clays are capable of jointly adsorbing most of atmospheric gases as it is so cold. Wetting of such samples, like was done in the chemical experiments in the Viking (from 1976 onwards) and Phoenix (in 2008) Mars lander missions, will bring about massive gas desorption of both CO_2 and O_2 , this gas release even mistaken for being due to biological activity (Figure 2.2).

8) 1 part per billion of *volume* (rather than 10^{-9} of mass).

9) 1 part per trillion of *volume* (rather than 10^{-12} of mass).

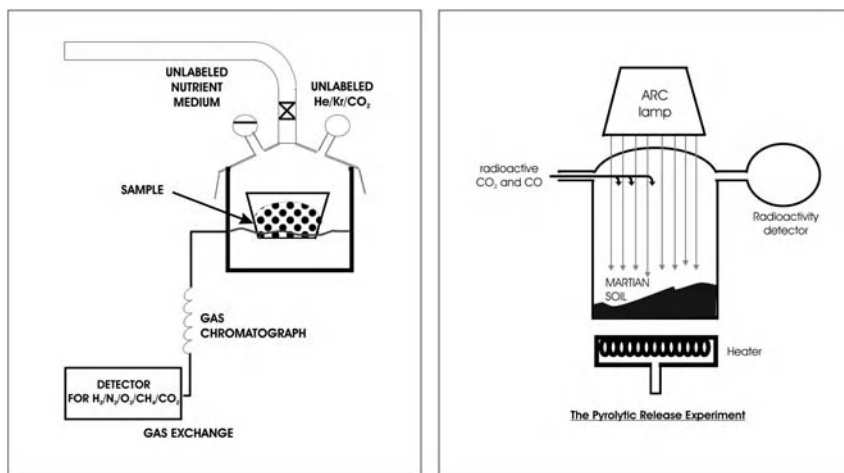


Figure 2.2 Left: The *gas exchange (GEX)* experiment done on Mars soil samples in the 1970s. Addition of water causes desorption of both CO₂ and O₂, the latter originating possibly from H₂O₂ or peroxocarbonates. Perchlorate is also present but is stable in solution still. The traces of methane now known to be present in Martian troposphere and to be vented from certain contrived regions could not be detected then and there by the GEX apparatus. Right: The *pyrolytic*

release (PR) experiment done on Mars soil samples in the 1970s. Radioactively labeled gases are permitted to get adsorbed, undergo possible photochemical (or photosynthetic?) transformations there and become thermally desorbed thereafter. Pictures by Darling D. (no year given): *The Encyclopedia of Science, Astrobiology, Viking gas exchange (GEX) experiment (left) and the Viking pyrolytic release (PR) experiment (right)*.

So Mars now is too cold to maintain a really thick atmosphere. On Earth ($T \approx 300\text{ K}$), the situation just is intermediate, both limiting adsorption and allowing for uptake of acidic gases (all CO₂, SO₂, HCl and photooxidants like HCOOH) by soil or airborne particles simultaneously. This is not to say that adsorption will not play a large role in air-soil interactions—both natural and pollution-induced—on Earth also:

- 1) Solids like titania (rutile) are so effective sorbents in photoelectrochemistry that CO₂ produced on them by photooxidation will not readily be cleaved to the gas phase but stick and block further photooxidation unless for wet (dew) desorption; even though photoelectrochemistry on TiO₂ and other photocatalysts will readily operate vs. a gas phase (rather than an electrolyte solvent) also, this retaining CO₂ will occur up to $>150^\circ\text{C}$;
- 2) Adsorption of atmospheric gases is the starting step of chemical attack on both ceramic, carbonatic and metal interfaces exposed to polluted air.

Indeed there is evidence for photochemistry to occur and be promoted by mineral particles in the troposphere (Zamaraev, Khramov and Parmon, 1994).

There is more to be learned from this comparison among the three larger terrestrial objects¹⁰⁾. While the two extreme states represented by (contemporary) Mars and Venus are self-stabilizing though obstructive to life at the surface in either case that of Earth is more labile; it is entirely possible to cause massive changes into either direction by either large impacts or human activity. The extinct huge dragonflies (*Meganeura monyi*) of Carbon ages suggest that most of then Earth's atmosphere was removed by some sediment interactions soon afterwards in an obviously irreversible fashion (now, the atmospheric lifetime of N₂ is about 15 mio. years). Hence, be careful!

This statement extends even to some of the most abundant components of Earth's atmosphere, due to the considerable reactivity of dioxygen. Its average lifetime in the troposphere is just 3000 years, with lots of both inorganic and organic materials around to absorb it by oxidation once they get uncovered due to erosion, digging or mining.

2.2.1.1 The Reactor Concept Applied to the Atmosphere

Earth's atmosphere, acting as a reactor like those of other planets or moons also, is driven into nonequilibrium states by an external energy source, that is, solar light¹¹⁾. Active volcanoes (giving access to thermal non-equilibrium with the atmosphere and reducing capabilities of the upper mantle) and biology (photosynthesis, with or without cleavage of water, plus anaerobic degradations of biomass so produced) provide considerably larger deviations from the local thermodynamical (chemical) equilibrium (LTE) than can be found on either Mars (traces of CH₄ from several unidentified surface sources besides O₂, O₃, H₂O₂, HNO₃ and a surface composed of almost fully oxidized Fe oxides, perchlorates and probably peroxides or superoxides) or Venus (H₂S and CO besides some O₂): on Earth, there are lots of O₂, plus traces of O₃, H₂O₂, HNO₃ to co-exist with some methane, formaldehyde, CO, and molecular hydrogen (cf. Table 2.2).

- 10) Here "terrestrial objects" are planets and satellites of almost planet sizes – rather than dwarf planets – being distinguished by some solid surface (which is essential for the sorptive and chemical interactions discussed above to occur). Including the four innermost planets, and seven large satellites, their total number is 11. Among those, only the three planets compared above and satellites Titan, Triton (orbiting Saturn and Neptune, respectively) sport substantial atmospheres, but do so at surface temperatures (some 94 and 38 K, respectively) where, beyond adsorption, even condensation of common atmospheric gases becomes an issue.
- 11) In the outer solar system, there also is atmospheric non-LTE (local thermodynamical [chemical] equilibrium) in both smaller (satellites of 1500–5300 km

diameter) and larger (gas planets Jupiter, Saturn and Neptune) bodies but for different reasons, namely: (i) radiochemistry (cosmic rays, accelerated particles in planetary magnetic fields) and (ii) upward mixing of species which are formed in hot, H₂-rich (several 100 bar) and H₂O vapor-containing regions of the latter atmospheres. Thus "high energy" compounds like CO (from water–gas shift reaction among CH₄ and water) and labile hydrides of P, As or Ge (PH₃, AsH₃, GeH₄) turn up in the observable stratospheres and tropopauses (≈uppermost cloud deck) of Jupiter, Saturn and Neptune (the stably stratified, almost non-convective atmosphere of Uranus does not afford such compounds) while others like HCN, HC₂CN, HCP are formed radiochemically.

Obviously, non-LTE mixtures are metastable at best (and concentrations which remain approximately constant with time despite constant energy and matter inputs give proof that they actually react with each other) and the corresponding chemical reactions (e.g., in Earth's atmosphere, between O_2 and H_2) might release considerable amounts of energy. Given this, the actual reaction rates are such that: (i) non-LTE can still be inferred from chemical compositions but (ii) the *atmosphere* will not explode even during thunderstorms providing appropriate sparks because pileup is kept way short of ignition limits by the above turnover: now, there are some 1.8 ppm of CH_4 and 0.5 ppm of H_2 besides of 21% O_2 in Earth's atmosphere, which "safely" compares to lower ignition limits of some 4% hydrogen compounds in either case (i.e., more than four powers of ten more). Biology and volcanoes yet can maintain considerable non-LTE on Earth [the sources of CH_4 on Mars, *perhaps* biological, are fully enigmatic by now, as is its small lifetime of few weeks (rather than hundreds of years) which precludes complete global Martian mixing].

Some chemical reactions in the atmosphere will influence structure and optical properties of the atmosphere also, namely those which produce condensed-liquid or solid-particles, aerosols and hydrometeors. These originally tiny particles will grow by sticking to each other, condensation of less volatile components (water, ammonium salts, acid hydrates) on their surface and other physical and chemical processes. Such aerosols cause severe health hazards when they are inhaled, getting deep into the lungs to stay there if the particle size is "appropriate"¹²⁾, thus becoming toxic and carcinogenic even if the "bulk" components are harmless [is there anything to fear with Mg silicate unless it forms needles of about 1 μm length (asbestos)?]. Parts of this aerosol formation are due to substances, precursors and their reactions introduced to atmosphere by humans; accordingly this way of forming smog can be influenced by man also, demanding control or abolition of the respective inputs into air. While abolition is subject to legislation, controls of both inputs and of a possible ban are tasks of technology once again. Methods to keep or get air clean or purified will be discussed later in this book (Section 4.1).

As mentioned above, the principal reason and source of energy for producing non-equilibrium in the atmosphere and subsequent reactions among components thus created is light and UV radiation. It penetrates the atmosphere to become partly absorbed, with the latter share causing chemical reactions and other processes (Grothus-Draper's law: only radiation which is absorbed in some system can cause photochemistry there; Hennig and Rehorek, 1987). It is commonplace in atmospheric chemistry to use a broader classification of photochemical transitions and to distinguish between *direct* and *indirect* photochemical processes where:

- Direct processes are such induced in some molecule by absorption of light at this very site [e.g., splitting of NO_2 or ozone into O_2 (NO) and an excited oxygen atom].

12) The critical size range is between 0.3 and 5.0 μm : while larger particles are removed from the bronchia by flimmer epithelion, others (<300 nm) simply get exhaled again as if they were gaseous themselves.

- Reactions caused by species which or their precursors are produced in a photochemical manner are called indirect.

OH and few other radicals, like NO_3 (which is not a photoproduct but so photolabile that it will persist only during night) provide oxidation of the largest share of organics and other reducing compounds in the atmosphere. While chemical fires “operate” at some 1400–2000 K (typical ignition levels about 800 K), that is, some seven (about three) times more than the temperature of the troposphere, there thermochemical steps are possible which create or reproduce reactive radicals which in the atmosphere rather must be provided photochemically, that is, in an indirect manner.

Since there are sizable activation barriers for reactions among even-electron-number species (rather than free radicals), radicals are involved in most transformations which occur rather fastly in the atmosphere (which is rather cold¹³). If substances neither undergo washout by rain, snow, or fog, nor react with the above radicals (with NO_3 being pretty selective), they will persist in the troposphere and above for tens to millions (N_2) of years. Perfluorinated compounds such as CF_4 , SF_6 , CFCHs, but also CO_2 , N_2O cannot react with OH (there is no H which could be abstracted, and bond energies in HO–F or H– O_2 are way smaller than in C–F bonds) and thus last very long, as does N_2 which only is converted into NH_3 biologically and into NO_x by thunderbolts (Kasting, 1993).

2.2.1.2 Structure and Layers of the Atmosphere

Regardless of geographical latitude or solid land or ocean being underneath, there is some constant structure of the atmosphere consisting of several layers (Figure 2.3).

Next to the ground there is the troposphere (literally, “nearby atmosphere”), extending upward vertically to some 9 km (polar regions) to 17 km (tropical belt). There is fast vertical transport in either direction by convection. As a result, cool-down of up-rising and thus expanding (decreasing external pressure) bodies of air occurs in a manner which is almost adiabatical, producing a temperature decline of some 7 K/km vertically which makes water vapor in this air body condense,

- 13) At still lower temperatures ($T < 100\text{ K}$), activation barriers must be omitted altogether for reactions to occur readily, essentially reducing the possible chemical pathways to reactions between neutrals (even- or odd-electrons) and cations (or recombination of the latter with electrons) like:



in stratospheres of outer planets (Saturn–Neptune), dwarf planets (Pluto,

Eris), satellites (Titan, Triton) or interstellar gas/dust clouds. These may yet afford a multitude of familiar molecules. Devices which excite smoke/gas mixtures by electron jets make use of the same kind of reactions which need no more thermal activation once ionizing radiation afforded the above precursors. Thus NO_x and SO_2 will react with O_2 to be precipitated into solid nitrates, sulfates when metal cations and electrons for recombination are available.

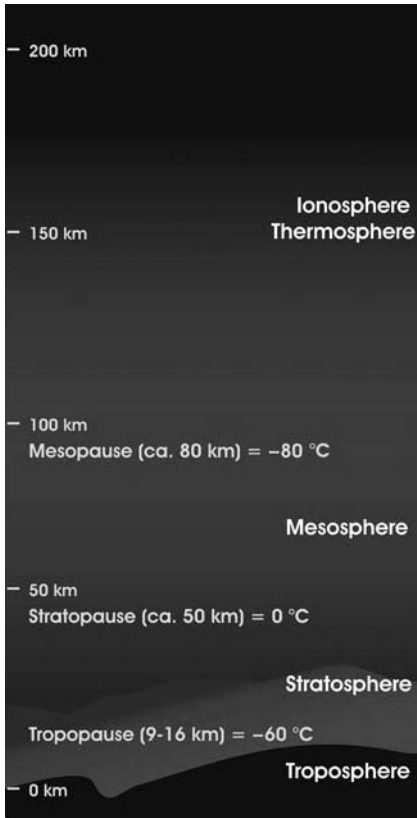


Figure 2.3 Structure of the atmosphere. Courtesy: data by Helmut Gröll.

producing clouds¹⁴⁾ and eventually precipitation (rain, hail, snow). Both effects influence radiation and heat balance of Earth since there is an onset of convection only if vertical heat flow is larger than that which could be handled by mere heat conduction along the gas phase (self-organization in irreversible thermodynamics), in addition:

- Heat energy consumed to evaporate liquid water at the (soil, lake, ocean) surface) is re-released somewhat higher up during condensation, cloud-formation, causing vertical transport of heat energy.

14) Both glider pilots and large birds of prey are aware of this effect: they use the presence of typically shaped clouds to spot regions of thermal upward air current which make them soar and continue flight

without muscle or engine efforts, with those upwind fields sometimes even extending over long distances rather than having contrived regions of airlift (in German, "Wolkenstrasse").

- Clouds reflect radiation in either direction (up and down), thus decreasing both uptake of energy from outer space and the radiative cooling of soil during night.

The troposphere is limited and covered by the tropopause where there is no convection, slowing down the further vertical uprising of long-lived chemicals from soil and lower atmosphere. Only compounds which can stand attack by radicals and (considerably more intense) UV radiation for some 10 years at least, will make it into the stratosphere. Equal lateral (horizontal) mixing in the troposphere takes a little less time, some 3–5 years, which means that passing 15 000 km or more parallel to the ground is faster than rising to some 15 km vertically. As there is no convection in the tropopause (and neither in the lower stratosphere), compounds produced (e.g., ozone) or released (thermal destruction of meteorites) even higher will neither undergo downward mixing, unless large particles form.

As mentioned before, the few kilometers of tropopause are covered by the stratosphere which owes its name to its being stratified, that is, being not convective, either. One effect which blocks convection is upside heating by radiation absorption in the ozone layer. Notably, there are only traces of water vapor in the stratosphere, hence there is no prolific source for OH radicals which form from water by either reaction with $O^1D^{15)}$ or (in large altitudes) direct photolysis. The warmest region, the stratopause at some 50 km height, blocks vertical mixing like the tropopause does. The next layer is called mesosphere, containing the turbopause where the atmosphere starts to unmix, making the heavy gases nitrogen, argon and oxygen sink down whereas volume shares of very light ones like hydrogen and helium (each a few ppm close to the ground) substantially increase, as do those of ions (“ionosphere”). The turbopause, also known as mesopause, is the coldest part of the entire atmospheric column, at some 180 K. Higher up the temperature—if it still makes sense to call the thermal status of this almost-vacuum a temperature—then rapidly increases up to some 2000 K. This is the region (90–95 km above) where small meteorites are heated and destroyed in the atmosphere, giving away water, methane, and some organics like HCN, HCHO, besides metal ions. In recent times, there is an additional phenomenon directly above the turbopause (at 82–85 km) which was not observed until much after the onset of industrial pollution: noctilucent clouds, being a chemically ill-defined aerosol both illuminated still much after sunset and excited by the outskirts of the ionosphere. The high temperatures at the uppermost traces of the atmosphere vastly increase the chances of atoms and even molecules to be accelerated up to second cosmic

15) O^1D denotes a certain, highly reactive excited state of the oxygen *atom*. As a rule (Hund’s rule) electrons are distributed among orbitals outside of chemical bonds in a manner as to occupy the utmost number of different orbitals, thus each but singly, and it takes additional energy to combine two electrons (the maximum number) in one given orbital. The number 1 denotes a singlet state, lacking any unpaired electrons, like in a stable

molecule (for comparison, the ground state of atomic oxygen is triplet O^3P having two unpaired electrons). P and D are symbols for principal quantum numbers attributed to the electrons. Spin pairing in O^1D spells taking up the excess energy which can—and usually will—be released when hitting another molecule and react with it: water vapor produces two OH radicals, whereas in liquid water H_2O_2 is selectively produced.

velocity, directly escaping the grip of Earth's gravity at v (velocity) > 11 km/s if there is no more scattering [>10 km free wavelength ($p \leq 10^{-11}$ bar) before hitting another molecule]; in addition, the ions interact with the magnetic field of Earth and are thus removed. This region is called exosphere, linking Earth to outer space by some steady though small loss of matter from the upper atmosphere¹⁶.

Anthropogenic, non-condensable compounds like tetrafluoromethane (CF_4) and hexafluoroethane (C_2F_6 , both from aluminum smelters; $T_{1/2} \gg 10000$ y) will get into such heights in the centuries and millennia to come, with C–F bonds to be cleaved when radiation of $\lambda \leq 195$ nm gets there (upward the stratopause). But what will happen to fluorine atoms thus liberated? Except for the remains of burned meteorites, water ice and some ozone there are no reaction partners anymore, which could influence the lower layers. Hence F atoms eventually react with hydrogen-containing compounds (all these including water because the H bond dissociation energy of hydrogen fluoride (HF) is larger than that of every other H compound including H_2O , HCN, and 1-alkynes), without a chance for HF thus and there produced to adsorb or react with dust particles¹⁷ or water ice, respectively. Lacking reaction partners as possible sinks, HF will enrich up there, to levels of ≈ 1 ppb around the Antarctic polar vortex, while there are only 0.1–0.2 ppb in moderate latitudes of the Northern hemisphere.

Starting with the ionosphere upward, there will be not only ionization caused by solar extreme ultraviolet [EUV (photocleaning extreme ultraviolet), VUV (vacuum ultraviolet; <200 nm)], particle (solar wind) and X-ray emissions, but of course processes are induced likewise which take less energy than ionization, that is, electronic excitation of the few atoms, molecules and ions still around up there. The result is a really good show—aurora borealis—, emission like in neon ads or other gas discharge systems, with polar lights giving information on species being rather abundant in the given layer by their respective colors and optical, UV spectra. Some particularly beautiful aurorae are given in Figure 2.4. The upper two photographs show different colors of emission arranged in a typical way (green emission downward, reddish-pink above) which corresponds to layering of the atmosphere much above the turbopause (which is located below the basis of the ionosphere).

2.2.1.3 The Atmosphere Acting as a Reactor: the Specific Role(s) of Highly Reactive Species

The abundant, trace or ultratrace gases and vapors listed in Table 2.3 strongly differ with respect to all chemical reactivity, volatility [boiling points between 4.2 K (helium) and 611 K (sulfuric acid)], sources and sinks.

16) The light gas helium is most prone to this rather than hydrogen, which is partly retained by chemical reactions with heavier atoms. The ≈ 5 ppm of He next to Earth are reproduced by radioactive α -decay within a few hundred kiloyears; if it were actually retained, He would now be the most abundant atmospheric gas besides N_2 .

17) Silicate dusts react with hydrogen fluoride (HF) to yield gaseous silicon fluoride SiF_4 while carbonates afford solid fluoride salts (+ CO_2); hence only the former kind of dust will be cleaved.



Figure 2.4 Polar lights (aurorae) are induced by electronic excitation of molecules, atoms and ions in the uppermost atmosphere and subsequent emission; accordingly, their colors and spectra reveal the composition of the upper atmospheres (there are also aurorae on Jupiter and Saturn). The principal sources of exciting particles are solar wind and cosmic radiation, with O, N and H species producing the colors. Red aurorae (right upper picture)

will be seen only above 200 km since the corresponding states of oxygen atoms will emit this light only if there are no more collisions among O^* and other gas particles. Blue emissions (left upper picture) are due to N_2^+ , the—usually brightest—green emissions are due to (allowed) transitions of atomic O once again. Photographs by courtesy of: Oliver Eßer, Foto Media (www.fotomediaweb.de).

Table 2.3 Abundance, origins and average lifetimes of free radicals pertinent to atmospheric chemistry.

Gas	Share (ppt) ^{a)}	Origin	Lifetime (s)
$\bullet NO_3$	Ca. 10 (during night only)	$NO_2 + O_3$; $HNO_3 + OH$	
$\bullet OH$	0.02–0.03	$H_2O + O^1D$, $H_2O_2 + hv$, $HONO + hv$	<1
O^1D	Variable (10^{-5} – 10^{-4})	Ozone photolysis	Ca. 10^{-6}
$\bullet OCl$		UV irradiation to seaspray	

a) ppt = parts per trillion (1 in 10^{12}): 1 ppt = $2.5 \cdot 10^7$ molecules (radicals)/ cm^3 .

Anyway, reaction rates (turnovers) are limited (finite) due to:

- Finite rates of collisions (there cannot be more intermolecular reactions than collisions, usually much less) with either reaction partners or molecules/atoms which provide or absorb (kinetic/thermal) energy;
- (UV) radiation flux and simply, eventually:
- Availability/abundance of reaction partners.

If there are highly reactive compounds which contribute significantly to the biogeochemical cycle of some element by themselves (e.g., SO_2 or NH_3), there is a risk to "overload" the natural [directly or indirectly ($\bullet\text{OH}$, $\bullet\text{NO}_3$)] photochemical cleavage processes, causing the corresponding substance to accumulate in the atmosphere and produce chemical or toxicological secondary problems (irritation, burns). If turnover and thus cleavage rates are very small, accumulation is at hand also like with CFCs which are hardly involved in C or Cl cycles below the stratosphere. Only there they are coerced into reaction by photolysis.

Most of the OH radicals formed by photochemical transformations involving ozone, nitric acid or hydrogen peroxide will react with CO and hydrocarbons. Although OH is consumed—forming water or H atoms thereby—there will be organic radical byproducts which are capable to add to unsaturated compounds (alkenes, alkynes; e.g., terpenes from forest vegetation), forming ever larger radicals one by one, much like in technical polymer (plastics) syntheses. The airborne polymers thus created will give rise to aerosols (Los Angeles smog). Concentrations of highly reactive (radical) species are given in Table 2.3.

Now we embark to estimate the relative contributions of certain compounds which form components of the atmosphere and of (biogeochemical) cycles in which they are involved, simply by comparing average lifetimes to ambient concentrations. We restrict this to common non-metals N, C, Cl, and S although, of course, this holds for all elements which exist in volatile or other airborne species, including not only most other non-metals (except boron), but also mercury and other metals which are volatile or undergo ready biomethylation.

Forms which react but sluggishly, like N_2 , may readily enrich but need not be processed at similar rates [measured in megatonnes of element (here: N)/year globally] like ammonia, N oxides or some organics such as acetonitrile CH_3CN . A global emission of 500 000 t, which is typical for common boost gases like for evaporation, spill losses of the most common solvents and for secondary biological responses to eutrophication (which causes enhanced release of gases such as methyl chloride CH_3Cl in shallow marine waters) is equivalent to 16 kg/s globally. If a substance is emitted in such amounts, at a processing/cleavage rate $\ll 1$ ppbv/year, it will enrich [the cleavage rate of CH_4 is ≈ 300 ppb/year, but its release from agriculture (cattle breeding, rice paddies) and faulty natural gas pipelines is correspondingly larger]. For CO_2 , the *additional* anthropogenic input is about 8 bio. t/year, causing an increase of several ppm (rather than ppb)/year even though some 70% of the input are sequestered by either photosynthesis or marine absorption. The same way of reasoning is applied to several other elements which are

Table 2.4 Concentrations, atmospheric (tropospheric) lifetimes and average turnover rates of pertinent N, C, Cl and S compounds in Earth's atmosphere. For additional explanations, see text and footnote.

Element	compound	Concentration <i>c</i> (ppb)	lifetime <i>t</i> (years)	<i>c/t</i> (ppb/ year)	Stoichiometric factor	Turnover rate
N	•NO	3	0.001	3000	1	3000
	NH ₃	<20	0.01–0.03	700–2000	1	700–2000
	N ₂	7.81*10 ⁸	16*10 ⁶	49	2	98 ^{a)}
	HNO ₃	1	0.02	50	1	50
	•NO ₂	3	0.1	30	1	30
	N ₂ O	310	170	1.8	2	3.6
	HCN	0.1–0.9	0.2	0.5–4.5	1	0.5–4.5
S	SO ₂	<20	0.01	<2000	1	<2000
	H ₂ S	2–20	≤0.01 (0.008)	Ca. 200	1	Ca. 200
	(CH ₃) ₂ S	0.09–0.15	0.0015	60–100	1	60–100
	H ₂ SO ₄	0.1	0.02	5	1	5
	COS	0.5	>50	<0.01	1	<0.01
	SF ₆	3.6	3200	0.001	1	0.001
Cl	HCl	1.5	0.01	150	1	150
	CH ₃ Cl	0.6	1.5	0.4	1	0.4
	CHClF ₂	0.11	12	0.009	1	0.009
	CCl ₄	0.12	60	0.002	4	0.008
	CF ₂ Cl ₂	0.3	150	0.002	2	0.004
C	HCHO	<10	0.0005 (daytime)	<20000	1	<20000
	CO ₂	3.7*10 ⁵	100	3700	1	3700
	CH ₄	1800	4.5	400	1	400
	CO	10–200	0.4	25–500	1	25–500
	HCN	0.1–0.9	0.2	0.5–4.5	1	0.5–4.5
	CH ₃ Cl	0.6	1.5	0.4	1	0.4
	CH ₃ CN	0.8 (0.082)	20 (0.5)	0.04	2	Ca. 0.1
	COS	0.5	>50	<0.01	1	<0.01

- a) The anthropogenic turnover rate of N is about 500 ppb/year, that is, five times as large. It is caused by hydrogenation of N₂ to produce ammonium fertilizers, explosives, and fuels (hydrazine). N processing at a total six times the “natural” rate has caused some 30% of the inorganic (urea) and organic nitrogen encountered in humans and cattle to have undergone (technical, Haber–Bosch) N hydrogenation at least once.

relevant to biochemistry also: C, S and Cl. Turnovers thus calculated are given in Table 2.4.

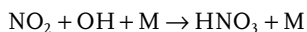
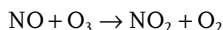
The *stoichiometric factor* corresponds to the number of atoms of the respective element tied up in a singly molecule, for example, four chlorine atoms on CCl₄ or two nitrogen atoms in nitrous oxide N₂O. When trying to make a matter balance like in the rightmost column, this becomes a multiplying factor.

How much material corresponds to a turnover rate of 1 ppbv/year? Earth's atmosphere contains a total of 36.1 mol/cm², given a pressure of 101 325 Pa, which

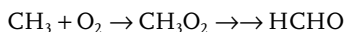
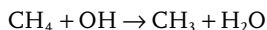
translates by gravitational acceleration to about 1.033 kg/cm^2 , to be divided by an average molar mass of 28.6 g/M . An annual turnover of 36.1 nmol/cm^2 corresponds (per second) to $1.14 \times 10^{-16} \text{ mol}$ (or 114 aM/cm^2), which translates into 580 M/s globally, given a surface of 510 mio km^2 or $5.1 \times 10^{18} \text{ cm}^2$. Most of the gases or vapors here to be discussed have molar masses of about 100 rather than the average 28.6, so 580 M/s translates into a global turnover (by chemistry, photochemistry or washout) of some 60 kg/s . Of course, differences in all temperature, optical and UV radiation fluxes and moisture levels/flows in different parts of the world may add up to local deviations of this global flux rates of several orders of magnitude. In the coldest parts of the Antarctic, even the noble gases krypton and xenon may become tied up in hydrates rather than remaining in the atmosphere, moist climates enhance washout of ammonia, hydrochloric, nitric or sulfuric acids, the latter of which is poorly volatile, moreover. Photolysis of aldehydes depends on near-UV quantum fluxes directly, with CH_3CHO being reactive only just redward of the clear-air transmission limit.

It can be seen from this balance that just a small part of SO_2 sulfur ever turns up as gaseous sulfuric acid, with most of oxidative chemistry already occurring in fog droplets. For nitrogen, ammonia and $\bullet\text{NO}$ ($\bullet\text{NO}_x$) are strongly involved in matter flows, to be distinguished from other N compounds hardly taking part or contributing to N-cycling, like N_2O and the organic¹⁸⁾ compounds HCN and acetonitrile, while turnovers from and involving N_2 or nitric acid are moderately involved (in between). N_2 is activated by the nitrogenase enzyme system of symbiotic nodules and cyanobacteria and by lightning bolts in thunderstorms. Besides (biogenic, from algae and phytoplankton) dimethyl sulfide, H_2S and SO_2 are mainly involved in S cycling in the atmosphere; COS is so stable that it propagates into the stratosphere. The carbon cycle essentially is based on the two thermodynamically stable compounds CH_4 , and CO_2 , plus, of course, oxidation intermediates of methane including HCHO and CO.

Hence, but few compounds of each element are significantly involved in cycling, similar rates suggesting them to be parts of a common reaction sequence, like with NO_2 and HNO_3 or CH_4 , HCHO and CO:

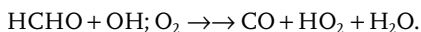
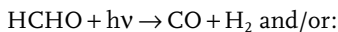


then washout or:



18) HCN here is related to organic substances due to its origin (pyrolysis of N-containing organics) and to its being the nitrile of an acknowledged organic acid (formic acid, HCOOH). Yet neither the anion, CN^- , nor cyanometallates are generally considered organic or organometallic compounds (like

with binary carbides such as methanides Al_4C_3 , Be_2C or acetylide CaC_2 , which afford the respective organics by protonation [hydrolysis] but different from metal carbonyl "organometallics" produced from metal [-compound] and "inorganic" CO).



Linking all the compounds plus OH radicals, O₂ to a common reaction chain, producing identical turnovers of the corresponding intermediates unless the latter are introduced by significant additional sources.

2.2.1.4 Chemical Peculiarities: Acidic and/or Hydrophilic Gases in the Atmosphere

Most trace gases (CH₄, N₂O, H₂, •NO_x, noble gases) are similarly (poorly) soluble in water and thus fog or rain droplets like N₂ or O₂ (≈10⁻³ mol/bar per kilogram), but there are notable exceptions: HCl, NH₃, HCHO; dissolution of all three gases in water affords 35–40% (ca. 10M) solutions at ambient pressure. However, actual atmospheric concentrations of these gases are in the ppb region, making concentrations in fog- or rain waters also about a billion times¹⁹⁾ lower than under pure gas.

Among the mentioned compounds, ammonia (NH₃) is the most abundant one (up to 20 ppb throughout larger volumes of air), with its aqueous solution being substantially alkaline. Nevertheless, pH values of airborne droplets get alkaline over longer periods of time only next to very large sites of pig rearing (megastables); thus, the effects of CO₂ and mineral acids are not balanced by NH₃ dissolution although NH₄⁺ salts are common in rain or fog waters. Notably, the first drops to fall after extended dry and sunny periodic use to be alkaline in fact, but this is due to the dust particles washed out thereby containing carbonates.

Some rarer gases (about 0.1–1.0 ppb) are vapors of strong acids, including hydrochloric, nitric and sulfuric acids, which, owing to the above solubility features, likewise enrich in precipitates, more so in snow or fog rather than rainwater. Then precipitation (or snow-melting) bring protons (acidity) into soils and surface waters. When and as these acids also attack surfaces, they cause all weathering (dissolution of carbonates and of the metal oxide “glue” of sandstone) of stones in the environment and buildings, corrosion of metal interfaces in architecture and vehicles [steel-made bridges often must now be abandoned much before their originally planned time of expiration (some 80 years)], and direct damage to biological interfaces, like etching of leaves and needles of plants. When the above acids attack interfaces or react with NH₃, they can produce aerosols [ammonium salts like (NH₄)HSO₄], convert solids into others (calcite into gypsum), with swelling or shrinking to further damage integrity of solid material meant to absorb mechanical burdens, or chain grain sizes in favor of smaller particles; sandstone will crumble when connecting Fe and Mn oxides are simply dissolved. Figure 2.5 shows corresponding damage on the stones of a church (St. Steven's) and epitaphs attached to it at Vienna, Austria.

19) Although Henry's law, stating a proportional relationship between solubility of a gas in some liquid and partial pressure of the gas above the liquid will no longer hold valid at solute mole

fractions of 0.1 or even more, yet deviations are small enough as to permit an estimate which only is wanted here: actually, [NH₄⁺] << 1 μmol/l in raindrops.



Figure 2.5 Damage caused by air pollution at Stephansdom (St. Steven's), Vienna (Austria), particularly at epitaphs. The main reason for damage here is SO_2 . When there are air oxygen, water vapor and possibly some catalyst such as nitric oxide, SO_2 forms sulfuric acid which degrades oxide crusts which make the glue of sandstone and convert calcite into gypsum which—like most sulfates as compared to carbonates—is

considerably more soluble in water. Metal surfaces might likewise be corroded to produce soluble sulfates. In addition, the molar volume of gypsum ($\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$) is larger than that of calcite CaCO_3 , making calcite interfaces like those shown here swell and crumble down eventually, destroying artworks (carvings, etc.) at the surface. Photo: © 2000 H. Riemer www.vienna.cc.

For many hydrophilic substances, including the above acids, ammonia, SO_2 , HCHO , their condensation product $\text{HOCH}_2\text{—SO}_3\text{H}$, hydrocyanide HCN , acetonitril, formic and acetic acids, dimethylarsinic acid (cacodylic acid, the principal As compound in the biosphere), attachment to condensed phases spells dissolution in fog or cloud waters and subsequent precipitation, this being the common key path for removal from the atmosphere. A closer look at Table 2.3 will show that, regardless of this identical mechanism, tropospheric lifetimes of these compounds differ somewhat (from hours to weeks, disregarding other sinks like photolysis of HCHO , NH_3). This is simply due to the fact that, even for NH_3 or HCl , not every collision of such a molecule with a liquid–water interface will make it stick to that interface and, thus, be dissolved in the droplet. Far from that, the probability of attachment here is about 5%. During such processes and by NH_3 reacting with acids HCl , HNO_3 , H_2SO_4 or HCOOH (in Los Angeles smog), ammonium salts and other aerosols form, making air a multiphase system beyond the presence of cloud droplets, with those and other (organic) suspended particles.

2.2.1.5 Air is a Multiphase System

Unlike liquids, gases are miscible in every proportion, regardless of chemical identity. Like mentioned above, chemical reactions among gases contribute to formation of aerosols. Although the gas phase in air is dominant with respect

to mass and particularly, volume share ($\gg 99\%$), the various solid and liquid condensed phases in air vary in both composition and chemical properties considerably:

- Aerosols are solid particles other than made of water ($\neq$ snow, hail), including soot, mineral dusts, biogenic particles like humus, peat, pollen, or bacteria, and products from chemical reactions like ammonium salts and ill-defined organic polymers, with size ranges from few nanometers (so-called Aitken nuclei; Wayne, 1991a) up to many cm in large hail grains. The size determines sink-down rates and thus the tropospheric presence of such particles²⁰⁾ which can last minutes up to weeks or even months.
- Suspended particles mainly consisting of water which precipitate given respective weather conditions are called hydrometeors in meteorology: rain, snow, hail, and sleet. Even if solid, these are not counted among aerosols.
- Gases, acidic and (almost) neutral liquid droplets, and neutral, acidic or alkaline solid particles of most variable compositions are involved in yet further reactions with gases present in air, sometimes even acting as catalysts. Of course, kind and chemical properties of some solid interface will determine the chemical processes which can occur or be catalyzed there²¹⁾. Whereas stoichiometric reactions will permanently change or even cleave the interface of some solid particle, catalytic ones (which means heterogeneous catalysis here) will chemically change gases or water droplets without permanently altering the particles.

What do such particles look like? The scanning electron microscope (SEM) picture (Figure 2.6) depicts a typical aerosol particle which is a conglomerate composed

- 20) Ashes and microsoot originating from large wildfires in Canada made their way once around the Northern hemisphere in 17 days which precisely agrees with the duration of round the world trips by gas balloons or montgolfieres. After Chernobyl, radionuclides (gases and aerosols) took ten days from Western Ukraine in a north eastern direction to the Bering Strait.
- 21) Acidic groups (Al^{3+} or Fe^{3+} in mineral dusts and clays, phenols, carboxylic acids in humic matter, crystal HNO_3 and HSO_4^- in liquid and solid particles) will bind and protonate (lock up to salts or ion pairs) ammonia and other alkaline reagents while carbonate dusts react with acids like HCl or HNO_3 . Nitrate salts thus formed are much less powerful oxidants or nitrating reagents (for PAHs, etc.) than free (even hydrated) HNO_3 , let alone the nanoparticles of acid rain which essentially correspond to “nitrating acid”. The latter

two reagents readily transform naphthalene and other airborne PAHs into both nitro- and nitrate-PAHs (Marino *et al.*, 2000; Vione *et al.*, 2004), while aqueous nitrate will do so only with rare earth elements (REE) ion catalysts, using different REEs like Nd, Eu, or Yb. Phenanthrene will react with NO_3 rather than OH, while 2-nitropyrenes and -fluorenes (not the 9-isomer) are most readily formed in urban (Athens, Greece) air (Marino *et al.*, 2000). Apart from this, nitrate photochemistry upon PAHs will cause hydroxylation (making PAH phenols, quinones) rather than nitration, with a turn in pathway to be expected only near $\text{pH} = 0$ (pK_a of HNO_3), that is, in extremely acidic fogs [formerly encountered in the Appalachian mountains (USA) and the Bohemian mountains (then the ČSSR)].



Figure 2.6 An aerosol particle combined of inorganic and biogenic sub-grains (scanning electron microscope picture, resolution 7.12 nm/pixel). © J. Huth, MPCh, Mainz).

of biogenic (spherical objects in center and to the upper right) and inorganic/mineralic (cube at upper left side) components. Such combinations are typical for soil grains and dusts suspended from soils.

2.2.1.6 Catalytic Processes in the Atmosphere

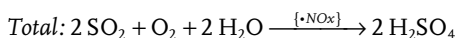
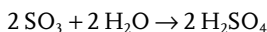
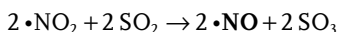
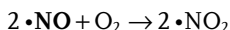
Accordingly to Ostwald's classical (1890s) definition a catalyst is a "substance which speeds up or just introduces chemical transformations by its very presence, without being permanently changed by them". The trace components of the atmosphere—both gas and dust—include quite a number of substances which are (or at least once were) also employed as catalysts in technical chemistry, among them iron and nitrogen oxides. In addition, some components of the atmosphere match substrates of technical chemistry which react at low (about room temperature) temperatures if catalyzed; hence, catalytic chemical transformation can be anticipated to occur in the atmosphere. Concerning ozone degradation in stratosphere, this is commonplace.

Up there, photoinduced catalytic reactions [*sensu* the classification of photochemical processes by Hennig and Rehorek (1987)] prevail, with FUV radiation just producing the very catalysts (chlorine and bromine atoms and monoxides ClO, BrO) from rather stable precursors (reservoir compounds) like CFCs, HCl and HOCl. As short-wavelength (FUV) radiation ($<230\text{--}295\text{ nm}$) is thus absorbed in the stratosphere completely, only radiation of $\lambda \geq 295\text{ nm}$ is available in the troposphere, while temperatures are considerably higher there. Accordingly, there will be a larger contribution from thermochemical transformations, involving heterogeneous catalysis at different kinds of dust, and much less photoinduced-catalytic chemistry, except for release of O atoms from O_3 , NO_2 and halogen oxides + BrCl from seaspray, which can be produced from local (surface-borne) sources at $\lambda > 300\text{ nm}$. In addition, both erosion and human activities, from agriculture to metal smelters, produce far more aerosols which could act as catalysts than ever present in the stratosphere (except when there were heavy volcano eruptions at

higher latitudes; e.g., Kamchatka, Aleut Islands). Both processes shall be discussed now with practical examples. If the consequences of catalytic reactions in the troposphere are unwanted, it is an obvious task of environmental engineering to reduce or abolish anthropogenic spreading of corresponding catalysts. In troposphere, there (fortunately!) is less UV irradiation available, moreover restricted to longer wavelengths of $\lambda \geq 295 \text{ nm}$.

1) Gaseous catalysts in the atmosphere

One important reaction of and among noxious gases which involves catalysis (of oxygen transfer from “innocent” O_2) is the so-called lead-chamber reaction which oxidizes SO_2 to sulfur trioxide, then hydrated to obtain sulfuric acid, by virtue of nitrogen oxides. This reaction can proceed via solid salt intermediate $\text{NO}^+\text{HSO}_4^-$ (“blue acid”) on virtually any solid surface including plant leaves/needles or minerals (turning calcite into gypsum) which can be etched by the strong acid produced. Lead chambers are no catalytic interfaces here but were used (from the eighteenth century onwards, the last sulfuric acid plants operating in this manner being abandoned in developing countries during the 1980s) to make reaction vessels which could then stand up to some 70% concentrations of aqueous H_2SO_4 and were easy to tighten and avoid venting of nitrogen oxide catalysts. The reaction proceeds as follows (catalytic species being boldly printed):



2) Solid catalysts in the atmosphere: soot and clay particles

Soot²²⁾, produced, for example, by Diesel engines, also displays pronounced catalytic activities in turnovers of organic materials (which may be relevant for its carcinogenic potential also, by the way), both loosely binding and then transferring functional groups and inducing redox processes. Either kind of process may convert less toxic compounds into benzene or certain, likewise highly toxic and carcinogenic PAHs. By binding free radicals like OH or NO_x , soot is converted into “graphitic acid”, an—unlike graphite fluoride C_8F or derived salts—ill-defined material, promoting recombination. In either way, it is probably far superior to oxides such as MgO or aluminosilicates (clay minerals) which have well-known and much-applied (Rothenberg, 2008) catalytic activities. Of course, clays are also introduced into the atmosphere by natural

22) Soot is not simply graphite, produced by ongoing dehydrogenating condensation of PAHs, but also contains *fullerenes*, the most simple (and abundant) of which are C_{60} and C_{70} , especially when derived from forest wildfires. Although rather expensive still

(comparable to the rarer platinum group metals) they are now intensely studied for their impressive catalyst and photocatalyst properties. Apart from fullerenes, soot produced by incomplete acetylene burning also displays high activity.

erosion, mining, and secondary activities like agriculture, burning pottery and corrosion of aluminum alloys.

3) *Mixed (multiphase) catalytic processes: decomposition of ozone*

Now (and for the foreseeable future) there is “too little” ozone in the stratosphere (although the Antarctic “ozone hole” is decreasing) to take effective shielding against shorter UV radiation far above the biosphere for granted whereas in the troposphere photochemical processes which use atmospheric pollutants make more of it than the biota likes [white-clover test (Heagle *et al.*, 1995), etc.]. It must be noted that ozone-decomposing processes are not fully identical in either layer of the atmosphere—mainly because of considerably different temperatures, temperature rate-dependences of crucial reactions and unlike preconditions for photoinduced or heterogeneous catalysis (see above) –, yet it is worthwhile to compare methods of technical ozone removal (produced, along NO_x , for example, in electrical discharges and open-air plasma-based technologies) and things which happen in troposphere to stratospheric decay paths. When passenger airplanes ascend up into tropopause or even lower stratosphere during long-distance flights at some 13 km (43 000 feet) above sea level [mainly during the so-called polar flights connecting Moscow or Central European airports with Anchorage (Alaska) or north east Asia destinations which actually take place at up to 85° latitude but anyway far above the ≈ 8 km Arctic tropopause, mixing in stratospheric ozone], the ozone introduced into the passenger compartment of an airplane fuselage by aspiring and compressing ambient (i.e., then, stratospheric) air must be removed to avoid irritation and intoxication of airplane passengers and -personnel. This is done mainly by passing the air—sucked in next to the jet inlets—over iron oxides which decompose ozone by heterogeneous catalysis.

Decay cycles mediated by radicals (oxides of chlorine and nitrogen) in the “neat” gas phase, rather than at solid dust particles, are relevant in both tropospheric, and stratospheric chemistry (Figure 2.7). As mentioned above, Cl oxides are afforded in the troposphere from seaspray photolysis and reactions of some chlorocarbons while in the stratosphere CFCs like CF_2Cl_2 and HCl undergo photocleavage of element (C or H)–Cl bonds. HCl, being highly stable in the absence of FUV radiation (far ultraviolet; <242 nm), alkaline compounds or solids, and of Mn oxides, is a reservoir substance, likely to pile up to some extent, as do anthropogenic CFCs, CCl_4 from marine biomass, or HOCl, and chlorine nitrate Cl-O-NO_2 , which both are rather stable if adsorbed on ice particles. The latter occurs in polar night conditions if local temperatures fall below 191 K (-82°C); during Arctic or Antarctic spring when there is sunlight again photolysis of the hitherto stable substances starts, and in addition HCl produces elemental chlorine by disproportionation with both Cl(+I) species HOCl and Cl-O-NO_2 , with the catalytic ozone destruction producing elemental oxygen O_2 .

- 1) $\bullet\text{Cl} + \text{O}_3 \rightarrow \bullet\text{OCl} + \text{O}_2$
- 2) $\bullet\text{OCl} + \text{O}_3 \rightarrow \bullet\text{OClO} + \text{O}_2$
- 3) $\bullet\text{OClO} + \text{O}_3 \rightarrow \bullet\text{OCl} + 2 \text{O}_2$

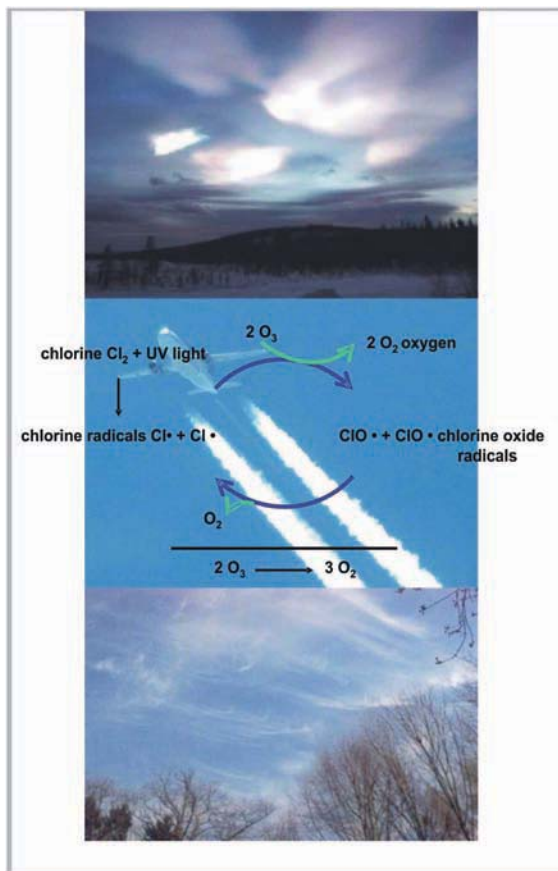
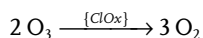


Figure 2.7 Most of atmospheric chlorine corresponds to fairly stable, even-electron species like HCl , HOCl and ClONO_2 rather than the radicals represented in the above box. Such stable compounds will accumulate in ice particles at sufficiently low temperatures and then undergo photolysis to afford Cl atoms and ClO radicals (the most abundant radical other than O^3P atoms between 41 and some 23 km above ground; Prinn, 1975; Lewis

and Prinn, 1984) like in CFC photolysis but this photolysis will onset at far greater wavelengths, where quantum fluxes are much higher. Commonly, stratospheric levels of ClO are some 20 pptv, except for the Antarctic where there is an increase to some 0.75 ppbv southward of 74°S (Wayne, 1991b). Photograph courtesy of: Prof. Zellner, Essen University, Germany.

Sum of steps (2) and (3):



Catalytic species are given in bold letters again.

With chlorine storage forms being enriched in solid ice particles, sudden onset of photolysis will translate into pulse-like inputs of ozone-destroying species and formation of corresponding “ozone holes” (lacking some 30–50% of the common

ozone levels) in Antarctic stratosphere during local spring (about October to early November). This will not happen in the troposphere because temperatures are much too high there everywhere except for wintertime central Antarctica to form these chlorine-storing ice particles.

Whether catalysts occur as gases or vapors or are bound to particles does not matter so much: being involved in reaction cycles, they will be reproduced on and on during ozone destruction until being consumed by some side reactions or (in troposphere) undergoing washout. Usually these side reactions are due to encounter of two radicals then recombining (a process with low activation barriers and a probability with the square of radical concentrations), awaiting new photoinduced catalytic activation to re-start the process.

Since hydroxyl ($\bullet\text{OH}$) and hydroperoxy radicals ($\bullet\text{HO}_2$) are similarly abundant but all Cl atoms, chlorine monoxide ($\bullet\text{OCl}$) and chlorine dioxide isomers much more rare than in stratosphere (Lewis and Prinn, 1984), the colloquial (Rowland and Molina, 1974) HalO -catalyzed ozone destruction cycle is hardly significant in the troposphere. Despite ozone being an irritant and toxic oxidant (much like elemental chlorine), it is not commonly removed by measures of environmental engineering rather than by enhanced venting of the site; f.e., iron oxide-based air filters are not used so far. Although N oxides cleave ozone in the polluted troposphere during night, they do not offer an alternative, being toxic irritants themselves, moreover involved in biological signaling (NO^{23}) and even producing ozone themselves in the daytime.

2.2.1.7 Chemical Reactivity, Growth and Removal (Precipitation) of Particles from Atmosphere

If weathering or reactions among ammonia and airborne acids like hydrochloric, nitric and sulfuric acids afford particles with abnormal, either very high (weathering, crunching of concrete) or very low pH values, these are going to be highly reactive. If particles with "acidic" and "alkalinic" interfaces meet each other and hit, they are likely to stick and form larger particles.

Beside acid-base interactions, photochemical processes (once again) contribute to particle formation: unsaturated hydrocarbons like terpenes (biogenic) and products of incomplete combustion—afford free radicals upon reactions with N oxides or OH, HO_2 (indirectly, from ozone), capable of adding to multiple bonds in yet other unsaturated hydrocarbons and thus grow, forming longer chains, O_2 addition also yielding peroxides which fasten up the process by chain-branching. Polymeres which are some crucial component of photochemical smog are thus made quite like in technical (plastics) polymerization. Additions of O_2 or N oxides yield highly reactive, irritant (among others, lachrymatory, even causing lung edemas) and corrosive secondaries, both fairly simply ones like aldehydes and

23) NO is a biochemical signal compound (much like glutamate) which means external administration by inhalation from polluted air will compromise inter-cell and inter-organ communication and metabolic

regulation, possibly even causing cancer. As the nervous system also depends on NO, external (atmospheric pollutant) NO also is neurotoxic.

formic acid (HCOOH), peroxy acetyl nitrate $\text{CH}_3\text{C}(\text{O})\text{--OO--NO}_2$ and other nitro compounds and more complicated, justly partly identified ones (let alone having a reasonable estimate of their toxicities). It is possible to discern this photochemical smog from particles and aerosols formed by acid–base reactions including ammonia simply by their respective colors: ammonium salts, including those thus formed in the environment, are bright white (colorless) whereas products of partial oxidation of organic materials are more or less reddish (cf. cosmochemistry, e.g., the orange cloud decks of Titan) and this component of Los Angeles smog likewise is orange-colored.

2.2.1.8 Conclusions Concerning Air Quality Integrity

To some zeroth approximation, controlling air purity is about avoiding smog formation. Hence processes must be controlled or (somehow) curbed which introduce the above chains of events. However, some of these pollutant gases (NH_3 , terpenes) are biogenic while others are delivered by volcanoes (parts of HCl , SO_2 , COS and CH_3Cl). Nevertheless humans are able to influence, control and reduce the emission of all S and N oxides, organic substances (including solvent vapors) and metal oxides (fly ash), with significant inputs now coming from vehicles (NO_2 , SO_2 from ship traffic using heavy oils in Diesel engines), domestic heating and agriculture producing rather larger impacts than single large combustion devices like fossil-fuel power plants, the emissions of which are solidly controlled and treated (in developed countries at least). As for agriculture, nitrates in fertilizers are released in N_2O (Pomowski *et al.*, 2011) and other nitrogen oxides by soil bacteria rather than undergoing complete reduction to ammonium ions or N_2 at least, if these soil bacteria feel there is too much of nitrate—and often they will think so much before the farmer does . . .

Nitrogen oxides are free radicals, with the oxygen-rich ones $\bullet\text{NO}_2$ and $\bullet\text{NO}_3$ being also sensitive to visible light. This is going to fasten up N cycling in the troposphere; there is additional evidence that eutrophication of Baltic Sea and corresponding phytoplankton blooms are due to airborne inputs of NO_x via atmosphere (which means that dissolution to water takes place within less than the few hours required to blow gases across this small sea) rather than the large rivers washing in dissolving nitrate. Although N oxides do hardly and slowly dissolve in neutral water, they will react with the somewhat alkaline seawater by disproportionation affording nitrate and nitrite, becoming bioavailable and thus causing eutrophication. At other (shelf) sites extensive growth of macroalgae (kelp) does combine with greenish phytoplankton blooms (California, Korea).

2.2.2

Water (Fresh-, Marine-, Groundwater)

Water is a special stuff, not just for its covering some 70% of Earth's surface (and some more 4% including the largest inland lakes²⁴⁾ and the ice sheets of Greenland

24) The biggest inland lakes, the Caspian Sea, Lake Baikal, and Lake Victoria, yet cover each <0.1% of Earth's total surface; the same holds for the permanently inundated parts of the Amazon river basin.

and Antarctica also consisting of water), with lots of living creatures thus moving inside rather than on or in solid earth or suspended/flying in air, but also owing to its chemical properties. It is a very peculiar solvent (see below)—and penetrates into those living beings much more deeply and without avoidance or exception, unlike the others: this principal solvent alludes to marine salt compositions still inside blood and similar liquids (hemolymph, xylem liquids). In aquatic organisms the border regions between the environment and in-body conditions are really floating, with water flowing through the gills, water making both the environment and most of the internal substance of the aquatic (limnetic and marine alike) organisms. Stomach and guts are also filled with a watery liquid, and digestion is tantamount to some combination of aquatic dissolution and hydrolysis of polymers, the latter promoted by the joint action of dilute hydrochloric acid and certain enzymes. External waters (can) interfere with both trace element budgets and osmoregulation in the body. Whereas certain organisms can or even must—for obligately anaerobic organisms—omit one of the other environmental compartments air or soil, contact with water cannot be abandoned for long although there are dormant states (seeds, eggs, spores) which can persist in an inactive state of anhydrobiosis.

2.2.2.1 Water as a Medium: Density, Optical and Thermal Properties, and Effects thereof on Biological Processes

The density of water is grossly equal to that of common biomasses like fats or proteins²⁵⁾, allowing to save energy in maintaining the vertical position/level in water as compared to air dwellers (which only can make use of thermal upwinds or terrain effects if not being very small). Therefore, and because access to dioxygen is improved by increasing pressure (like in air), aerobic living beings can inhabit all the levels of ocean and large lakes down to the deepest trenches, the hadal. However, getting food becomes an issue then: except for sites where chemoautotrophs provide primary production, deep-sea organisms eventually must rely upon what is sinking down. Although whale carcasses sinking to the ground provide just a few $\text{g C} \cdot \text{km}^{-2} \cdot \text{year}^{-1}$ ²⁶⁾ (maybe 1 kg/year before whaling was done at very large scales), they are a principal source, more so than dying

25) Unsubstituted hydrocarbons are distinguished by much lower, halogenated hydrocarbons by much higher densities than water. Concerning (anthropogenic) polymers, this fact is used in re-processing of plastics wastes: polyethylene and polypropylene (once again, pure aliphatic hydrocarbons), in a density range of $0.90\text{--}0.94 \text{ g/cm}^3$, ascend if immersed in water, unlike all the others, thus can be separated by aqueous flotation, then being reprocessed by melting as they are thermoplastic. By contrast, the density of nylon, for example, being a polyamide like all the proteins, exceeds that of water. Likewise aquatic animals take a small

amount of energy to maintain their level even in seawater ($\rho \approx 1.026 \text{ g/cm}^3$), unless parts of their bodies are filled with gases or body fluids contain dissolved (ammonium) salts of very low densities (giant squids; O'Shea and Bolstad, 2008). Now, there may be about 150 000 large whales, mostly fin and sperm whales, left in the oceans (from an estimated 2–3 millions before that paroxysm of whaling during the 1920s and 1930s), corresponding to some 7 mio. tonnes fresh weight, of which some 10% are organic carbon. Assuming an average lifespan of just 50 years from the few available data, $14\,000 \text{ t}$ [14 Gg (gigagram, $1 \text{ Gg} = 1000 \text{ t}$)] of

phytoplankton most of which is eaten before even leaving the photic zone. Considering the large depths of both oceans and deepest inland lakes (Baikal, Victoria), to our present knowledge there are just few species (notwithstanding the wealth of bacteria in sediment the variability of which we do not have even a sound idea of) around but in substantial numbers of individuals. Chemosynthesis and chemolithoautotrophy provide just local sources of primary production in the deeper seas (e.g., black smoker, see Figure 2.8); photosynthesis soon diminishes due to the transmission spectrum of water: although water (besides methanol, acetonitril) is among the solvents which are most transparent in the far ultraviolet (FUV, $<242\text{ nm}$), vacuum ultraviolet (VUV, $<200\text{ nm}$), regions, down to $\lambda < 200\text{ nm}$ in pure²⁷⁾ water, matters are quite different in those (visible) spectral regions exploited by photosynthesis: when you watch an object which is bright red at the surface sink down in a swimming pool, it appears dark brown when it sinks to just 2 m of depth, and it is almost black at some 5 m. Divers also notice that orange, yellow and green light (the colours following red in the shorter parts of the spectrum/rainbow) fade out, respectively, at some 6, 15 and 30–40 m of depth, even in very clear waters.

Being red or orange in bright sunlight will become a good method for fishes to camouflage against becoming prey just short below the surface whereas blue is kind of a signaling color. Owing to this varieties of blue which somewhat differ from the color of pure water thus are now often used to dye neoprene wetsuits for

C_{org} will trickle down annually, scattered over an area of some 360 mio. km²: 40 g/km²*year. Given the crucial role of this small but condensed supply for persistence of deep-sea fauna in between black smoker sites now, it is an interesting problem how corresponding organisms performed and sustained their livings in early Tertiary times (65–45 mio. years ago), that is, after extinction of large marine reptiles (Mosasaurs etc.) but before whales (*Pakicetus*, *Zeuglodon*, etc.) evolved. The black-smoker chemosynthetic oases were already or still available, for example, the copper deposits of Cyprus (for which the entire island got its name!) are partly due to fossil (middle Cretaceous) black smokers.

Phytoplankton sinking down is consumed so rapidly (mostly, above –100 m) that only small shares are available for detritus eaters in deep seas. This is why experiments to remove atmospheric carbon (CO₂) from oceanic atmospheres by fertilizing surface waters with Fe²⁺ actually causes plankton blooms but the intended transport of carbon from atmosphere to (presumably inactive)

deep-ocean sediments (“aquatic carbon burial”) essentially failed.

In the real ocean, there are various reasons for UV absorption even redward of 295 nm, the present limit of atmospheric transmission:

- Photodissociation of organic including DON compounds, with humic matter absorbing up to the visible;
- Photooxidation (charge transfer to solvent [or to dissolved O₂, NO₃[–]] of reduced metal ions and Br[–] (onset wavelength: NUV);
- Ligand to metal charge transfer (LMCT) bands of metal complexes;
- Rayleigh scattering by suspended particles which strongly increases at shorter wavelengths.

Concerning the photodissociation of S organics, sulfuric amino acids cysteine and methionine become a prolific source of highly stable carbonyl sulfide COS (besides of volcanoes, coal combustion) which then rises up into the stratosphere and influences the S cycle considerably.

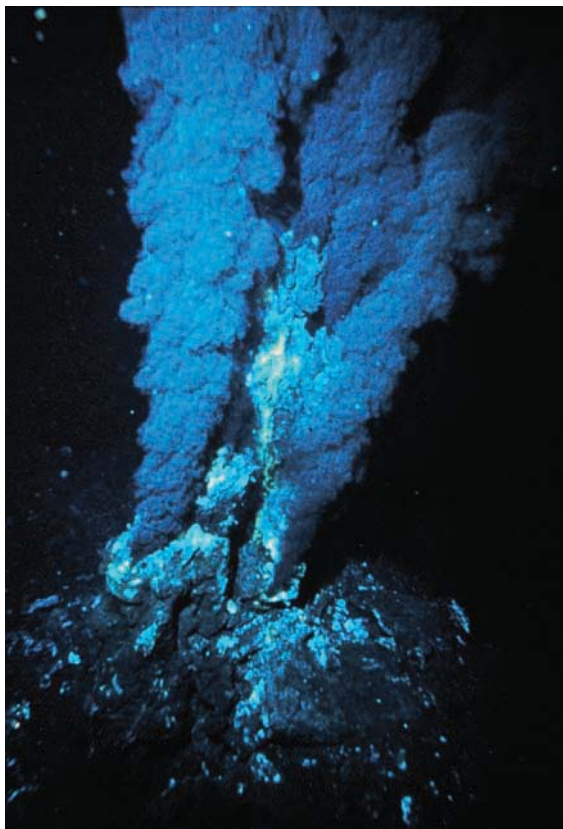


Figure 2.8 A “black smoker” submarine hot spring in deep ocean. The black suspensions are due to precipitations of metal sulfides. Photo: P. Rona, <http://www.photolib.noaa.gov/htmls/nur04506.htm>).

divers [while the colors of breathing gas tanks are regulated by national and international norms denoting the gas to be filled in (air, nitrox or trimix containing much helium), now being painted usually in white or yellow]. Yellow being the complementary color of blue would offer good contrast against blue or greenish background waters, but, as mentioned before, does so only above some 20 m.

This capability of both pure and “real” water to soon cancel out substantial parts of visible spectrum obviously determines the chances of any kind of photochemistry in deeper layers and corresponding deeper water volumes. Here, photochemistry denotes all “natural” transformations involving dissolved entities, including, for example, dissolved organic nitrogen (DON), PAHs, metal ions and their complexes (we shall re-address this issue upon considering photochemical means of water purification), technical measures to destroy pollutants, and photosynthesis. While the former two usually apply absorption bands in UV regions

and thus benefit from the transmission of water increasing with shorter wavelengths (viz., from red to UV light, see above), the case is different with photosynthesis. Chlorophyll and the other pigments of either green plant, algal (including zooxanthelle endosymbionts of stony corals) and bacterial (cyanobacteria, photothiobacteria) photosynthesis are green to turquoise in color, meaning them to absorb mainly red or orange light—which both fade out within a few meters below the surface. The corresponding spectral absorption maxima are at some 680–725 nm (red light, chlorophylls a–d²⁸⁾) and 650 nm, respectively (Figure 2.9).

Even if the water is extremely clear (Yucatan cenotes, atolls in Micronesia, some mountain lakes) and neither shore nor floating vegetation inhibits incidence of sunlight, thus photosynthetic productivity is considerably decreased already in waters as shallow as 3–10 m. The ultimate limit of photosynthesis is somewhere between 40 and 100 m depth. Of course, due to Grothuss–Draper's law, water plants including phytoplankton absorb light themselves by doing photosynthesis: only radiation which is absorbed can effect photochemical or photophysical transformations in the very absorbing substance or entity. Accordingly phytoplankton blooms do not extend deeper than some 3.5 m in eutrophic waters—further down it is rather dark already.

Owing to the large heat capacity of water, both diurnal and annual changes of temperatures are limited to thin surface layers of several decimeters or about 20 m, respectively. As it forms a highly branched network of so-called hydrogen bridges upon cooling in the liquid state, water is among the few compounds to expand by solidification [among elements, similar behavior usually is due to a concomitant metal- (dense arrangement of atoms in liquid)/semiconductor (branched array of covalent bonds), transition, for example, with germanium or antimony although few metals (Ga, Bi) behave likewise]. See some physical properties of liquid water in Table 2.5.

Hence ice floats on liquid water. The heat conductivity of ice is much smaller than with liquid water, precluding the complete freezing of lakes to the ground, rather maintaining thin ice layers even with steep thermal gradients: the maximum thickness of arctic sea ice (the Northern, freely drifting polar ice) is about 4–5 m, in rivers discharging into the Arctic Sea like Jenissei, Oimjakon (both located in Russia) or Mackenzie (Alaska) some 2 m late in local winter. These few m suffice

28) All the chlorophylls are Mg^{2+} complexes (rather instable ones, in fact) of porphyrines which differ in just some functional groups of the side chains around the porphyrine macrocycle. These functional groups (CH_3 , CH_3-CO- , $HCO-$, vinyl) besides the large phytane side chain significantly influence the absorption spectrum, exploiting radiation (orange and yellow light) which more deeply penetrates into water than red, making algae living in deeper waters mainly use these chlorophyll varieties. Anyway, given that the Sun (now) is a yellow star, with an emission

maximum shortward of 600 nm, one is posed to ask why plants are neither blue nor orange, making best absorption and photochemistry of yellow and greenish lights, now, in addition given the notorious instability of chlorophylls which causes complete photochemical desactivation within minutes unless introduced and protected in appropriate membranes. Probably this is a relic from early times of the Solar System when the Sun was cooler and less luminous, being orange rather than yellow then (Kippenhahn and Weigert, 1990).

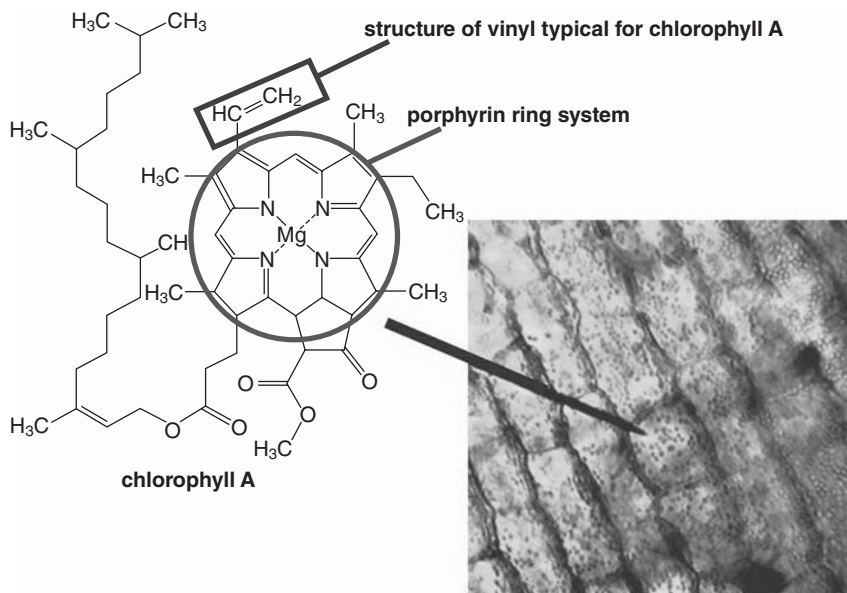


Figure 2.9 Chlorophyll is a Mg complex of a porphyrin absorbing red light, thus appearing green. Energy thus taken up is transferred to other compounds and eventually used to cause chemical binding of carbon dioxide and oxidation of water during oxygenic photosyn-

thesis (bacteria and cyanobacteria can also exploit electron sources for photosynthetic CO₂ reduction other than water—and more accessible in thermodynamic terms—including H₂S and Fe²⁺). See textbooks of plant physiology.

to maintain a winter temperature gradient of 40–70°C. Below the ice conditions are thermally and chemically fairly constant while its being transparent then stills permits photosynthesis, allowing the local biocenosis to survive winter-times.

2.2.2.2 Chemical Properties and Their Variation

Otherwise, water differs from air in not having relatively constant chemical conditions and properties concerning oxidative properties: while air consists to a substantial part of one, completely admixed strong oxidant (O₂), water itself (or, rather, the aquated proton H₃O⁺ at moreover very small concentrations—often <1 μM/l) is a rather poor one, just attacking base metals. Accordingly oxidative properties observed with ambient waters are rather due to dissolved species, including O₂ once again or nitrate ions, or some other anions like sulfate. Besides redox potential, pH may also change, with dissolved metal ions forming complexes with Cl⁻, humic acids, DON (dissolved organic nitrogen) and so on, or the complexes decomposing upon dilution by rainwater, increasing pH or photochemically. In water chemical elements respond by changing their modes of speciation, changing salt solubilities and in turn permitting to reconstruct parameters such as redox potential from the mixture of speciation forms observed. There are situations in

Table 2.5 Physical properties of liquid water (Sigg and Stumm, 1996, modified after Sverdrup, Johnson and Fleming, 1942 and Berner and Berner, 1987).

Property	Specifics and comparison with other liquids	Environmental implications
Density	Highest at +4 °C; expands when freezing	Limits freezing to surface regions, causes stratification of lakes in summer and winter seasons
Melting and boiling points	Much higher than in similarly small-molecule solvents	Water is enabled to persist on Earth ^{a)} as a liquid
Heat capacity	Largest heat capacity among liquids except for NH ₃	Avoids heating or cooling of larger water bodies to extreme temperatures
Evaporation heat	Extremely high	Limits heating of larger water bodies, allowing metazoans to survive
Surface tension	Large	Facilitates formation of droplets in clouds and rainfall
Light absorption	Very pronounced in IR, decreasing from red light to shorter wavelengths (see text)	Influences biological activities, including photosynthesis
Solvent properties	Dipolar, excellent solvent for salts and polar molecules but poor for hydrocarbons	Transport of dissolved matter in hydrological cycles, biota; formation of membranes, supportive structures

a) If one does (theoretically) “switch off” hydrogen bonding in water (see H₂Se, H₂Te) or reduces the 3-D framework of H bonds to a linear one (like that in methanol), both melting and boiling point will considerably decrease while the then range of liquid-state temperatures is less obvious either to increase (see CH₃OH) or decrease. Solvation of anions and thus salt solubilities would likewise be compromised. Anyway, liquid water would then exist only far out in the Solar System (Mars, Jovian moons).

which such events and/or the action of natural ligands (e.g., humic acids²⁹⁾) reduce the bioavailability of certain essential metal ions down to a level that certain kinds of organisms can no longer live in that water body.

Another important component and feature of natural waters is dissolved or colloidal, particulate organic matter (DOC, POC). This includes both short-lived compounds readily undergoing hydrolysis or microbial consumption and refrac-

29) This particularly holds for peat bog lakes; the only fishes which can persist there are either tiny, having abandoned most of their bony skeleton (cyprinids in Indonesia) or reduce exposition by breathing air (e.g., *Umbra krameri*).

Experiments in the lab also showed the effect of humic acid salts to severely reduce transfer of metals from sediment into green plants, forming metabolically hardly accessible species in the aqueous solution in between.

tory ones to stay in the liquid phase for long periods of time³⁰⁾, being rather inert against both bacteria and photodegradation, neither being precipitated by Fe(III) like polyphenols or by other metal ions (alkaline earth salts of fatty acids, polycarboxylic acids). Remaining suspended, this organic matter consisting of large molecules can then act as a sorbent and become transport vector and storage form for quite different xenobiotics some of which undergo irreversible binding to this polymeric POC matter. However, this irreversible attachment does not translate into “detoxification” in any case.

2.2.2.3 Water as a Multiphase System

Quite like air, water is a mobile multiphase system. This multiphase system consists of:

- The liquid;
- Suspended particles of various kinds—from mineral grains, clays, over organic matter up to entire organisms (plankton) –, besides this:
- Gas bubbles, especially in eutrophicated or agitated water bodies, and sometimes:
- Liquid particles not miscible with water (droplets of fats, oils).

There are matter exchange and chemical reactions to connect all these phases. Suspended particles may form by both chemical precipitation at sites where some parameters change suddenly, for example, both natural (river moundings, estuaries) and artificial (such as wastewater inlet pipes), or by physical agglomeration of colloids which happens at the isoelectric point, point of zero zeta potential (PZZP), when smaller particles loose their electrical (positive or negative) surface charge³¹⁾ (the PZZP depending on chemical composition of particles). Whereas particles in air are far denser than the medium, and consist of hardly volatile species, their aquatic counterparts almost match their embedding material in density, and moreover can be dispersed by chemical attack and simple dissolution. Hence water-borne particles are not simply going to grow until becoming too big to remain suspended and sink down, but can be partly or altogether dissolved by all

30) In marine waters, a large part of DOC, POC can be shown to be several thousand years old, probably being suspended or just briefly adsorbed for all the time in between.

31) Oxides, hydroxides and sulfides, but also other insoluble salts like phosphates like hydroxyapatite HAp [$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$] will respond to pH changes in surrounding waters by taking up (phosphate ions as a base) or giving away (OH as an acid) protons, causing the crystal- or particle interfaces to acquire some electric charge when deviating from isoelectric point pH = 7.0 for HAp (Zhang *et al.*, 2006).

Then the single particles no longer attract each other but repel electrostatically (push away); hence also very poorly soluble materials such as nickel sulfide NiS will no longer precipitate but form a completely stable colloid. However, it is possible to remove this surface charge once again by changing pH, electrochemical procedures or simple addition of salts the ions of which selectively adsorb to the particles rendering them neutral and ready to flocculate and precipitate fastly (with NiS, ammonium acetate solution is most suitable).

solvent attack to form ions, photochemical processes³²⁾ or/and biological attack (some bacteria produce ligands and deliver them to the environment which are capable to dissolve all Fe oxides, silica or the most stable of classical complexes). Besides of dissolution modification of the surface (“etching”) also is possible. In flowing water, sediments are much more readily re-suspended and transported than by air [fluvial and seashore erosion is quite commonplace while large-scale Eolian relocation of soils is peculiar (at least outside of China), producing a very specific, fine-grained variety of soil (loess)].

As water dissolves both ions and (polar) molecules, it can suspend also completely non-volatile compounds such as ionic salts or such which would decompose rather than go into some gas phase. Being dispersed in this manner also up to the surface, they become accessible to both photochemical and biological (comparatively insignificant in air) attacks.

2.2.2.4 Freshwater, Seawater, Osmotic Pressure, Redox States and Biology

Chemical processes now to be discussed which include all redox transformations, complexation and precipitation by various processes do not just influence and “modify”:

- Inorganic cat- or anions, such as phosphate, but likewise:
- Organic compounds if capable of either forming ions (sporting acidic or basic functional groups) or to coordinate to metal ions.

Humic materials can bind metals by means of various functional groups, such as 3-ketoenolate, phenolate, carboxylate or amino groups (Andelkovic *et al.*, 2006), itself undergoing quite a manifold of chemical and photochemical oxidation processes which produce oxygen-rich polymers. These are brown to black and extremely poorly soluble in water but may dissolve in polar organic solvents like dimethyl formamide. Especially in the oceans, dissolved organic matter (DOM) will remain suspended in particulate forms for very long periods of time.

When producing potable water from river shore filtrate or from other sources oxidants like chlorine, ozone or chlorine dioxide are used to effect purification and sterilization of the water samples. Then, of course, DOM which is also present in spring waters and escapes shore filtration lest for adsorption losses unchanged, will react with these oxidants, producing chlorinated organics³³⁾ including CHCl_3 from DOM and Cl_2 , ClO_2 , some of which (including chloroform which is among the most abundant) are also carcinogenic in humans. Other kinds of reactions and of pollutants also require subsequent precipitation or adsorptive removal of (then modified) organics if certain kinds of raw waters are used in certain environmental conditions:

32) Owing to the extremely low solubility of most heavy metals in ocean water photochemical particle degradation is essential in supply of marine life, for example, with manganese (Sunda and Huntsman, 1988).

33) The familiar strange, annoying smell in highly populated chlorinated swimming pools is due to N-chloro compounds containing N-Cl bonds, produced by attack of elemental chlorine on both urea and amino acids.



Figure 2.10 Water samples from a little lake in Saxony-Anhalt (Germany) taken before (left flask) and after (right flask) precipitation of polyphenols from carbochemistry ("anthropogenic humic substances") by addition of Fe(III). Cf. the precipitation of biogenic

polyphenols by the same agent: iron-gallic ink. Now the water is clear but yet cannot maintain fishes due to a substantial ammonia concentration level (photo: UFZ Leipzig/Halle, Environmental Research Center, "Sanierungsforschung").

A classical kind of anthropogenic humic matters are produced from (poly-) phenols like those originating during processing of lignite in carbochemistry: if funneled into open pits or small natural ponds, the result will be almost abiotic ponds into which light can penetrate no deeper than a few centimeters (Figure 2.10). However, it is feasible to precipitate such polyphenols by Fe(III) [like with iron-gallic acid inks], causing the water to become clear and allow life of organisms of all trophic levels again [e.g., the former 9-ha "Phenolsee"³⁴⁾ ("phenol lake"; 30 m deep) at Deuben, Saxony-Anhalt, Germany, which was effectively sanitized by this very procedure].

Depending on their structures, with $\log k_{ow}$ being crucial for partition among sediments (adsorption) and free water³⁵⁾, compounds with endocrine activities may also enrich in open or groundwaters. For example, 17- α -ethynylestradiol (EE2), the active component of most oral contraceptives (the "pill"), can now be detected at levels of some 10^{-10} g/l (close to the threshold for activity in many aquatic organisms) in most open-water samples and upper groundwater levels, yet it is an open matter whether this is due to recent emissions or, rather, residues from the highly dosed pills used in the 1960s and 1970s. As EE2 makes its way through sewage water treatment plants almost untouched, the only option to remove it here is adsorption to activated carbon or similar (non-polar) sorbents.

34) There still was some microbial activity in "Phenolsee"; even now, with sanitation by flocculation terminated in 2004, the ammonium levels in this water are too high to permit fishes to live there whereas aquatic insects (e.g., chironomid larvae) and water fowl do quite well.

35) For organics, there is an empirical relationship between water solubility and $\log k_{ow}$, namely (Fränze 1993):
 $\log p_{ow} = 4.5 - 0.75 \log S$ where S means aqueous solubility (mg/l). This relationship holds for hydrocarbons, PCBs, organic halides and aromatic acids alike.

Other endocrinically active agents like triorganotin salts or halophenols are accessible to electrochemical (anodic) oxidation also (Stichnothe *et al.*, 2005), or even become degraded by simple oxidants like in AOPs. Crude oil hydrocarbons, whether native or processed (gasoline, diesel, jet fuel), pose particular problems: secondaries produced after some spill by biochemical or photochemical processes tend to be both better soluble in water³⁶⁾ and thus more bioavailable (yet, less capable of accumulation) and more toxic (phenols, naphthols, hydroxyanilins) than the original products.

There are basic differences between limnetic and marine bodies of water, ranging from pH and, of course, ion concentrations up to features of geobiochemical cycles and physiological chemistry: fishes and other organisms must use certain strategies in (osmotically) hypertonic³⁷⁾ seawater, strategies which are rather different from those of limnetic creatures to achieve:

- Water supply of the organism;
- Excretion of ionic or ion-forming (like NH_3 at $\text{pH} < 9.5$) species against the difference of osmotic pressures.

Euryhalinic (capable to adapt to and sustain life in highly variable salt contents, for example, stickleback, desert cyprinids, some kinds of *Tilapia*), anadromic or catadromic fishes [which perform migrations between fresh and highly brackish or seawater related to reproduction (like salmon, common eel, or sturgeons)] are in a position to develop “double” structures adapted to either osmotic gradient in their digestive systems.

Few metals [alkali metals, Tl(I) , and alkaline earths heavier than Mg] form hydroxides which are readily soluble in water, while the others undergo precipitation already upon a moderate increase of pH (and thus OH^- concentrations) like observed when changing from common fresh- to seawater, except for amphoteric metals like Be , Al , Ga or Zn . For the latter, however, carbonates and/or phosphates are hardly soluble. Hence average concentrations of Fe , Mn , Co , Al , Pb and most rare earth elements in the oceans (Nozaki, 1997) are 40–15 000 times lower than in reference freshwater as defined by (Markert, 1994b). Unlike insoluble hydroxides, carbonates, phosphates or silicates, the existence of insoluble M(II)

36) At typical PAH solubilities of 10^{-3} (three-ring systems like phenanthrene, fluorene, or acenaphthene) to 10^{-5} g/l, which translates in the open ocean to 10–1000 t/km³, it becomes obvious that even very large spills like those recently in the Northern Gulf of Mexico (April, 2010) or 20 years ago in Arab Gulf can be dissolved altogether, with grave consequences: the non-polar organic fraction of such solution is readily absorbed by marine life, it is directly accessible to photochemistry (rather than just a thin surface crust of oil lumps

drifting around), and there is full neurotoxicity to animals, including narcotic modes of action.

37) Hypertonics are waters or other solutions whose osmotic pressure (loosely: the concentration/activity of dissolved ions or compounds) exceeds that of body sera or blood. When contacting some membrane, these are going to extract water from the body. Accordingly, it is meaningless and even dangerous to drink seawater when shipwrecked: human kidneys will not cope with large amounts of it.

sulfates at a substantial SO_4^{2-} concentration (9.4 mmol/l) does matter only with Ba and—under reducing conditions³⁸⁾ like in deeper parts of the Black Sea—europium Eu. Gypsum or strontium sulfate (strontianite) which latter is produced as a skeleton material by certain marine algae, are undersaturated in the ocean, thus going to dissolve if a structure made thereof is no longer maintained by active ion transport. In sewage treatment plants, a similar process is induced which brings about precipitation of ternary hydroxides after $\text{Ca}(\text{OH})_2$ (lime water) addition: Metal ions which form insoluble hydroxides—including amphoteric ones like Al which get locked up in ternary phases such as grossite CaAl_4O_7 —are thus deposited much as happens in river estuaries where there is also an increase in both pH and Ca^{2+} concentrations [in sewage treatment plants, acids formed in the process are also cleaved by $\text{Ca}(\text{OH})_2$ before discharging to the open waters].

Since seawater is a buffer system, conditions in seawater use to be much more constant than in lakes or rivers. Currents and larger average depths serve to reduce temperature differences and gradients also. The drawback is that marine organisms are much poorer in tolerating changes of the above parameters than limnetic ones use to be. Most critical, given the increasing partial pressure of CO_2 above the oceans, are implications of decreasing pH³⁹⁾. Another problem is coral bleaching, which happens by die-off of zooxanthelle symbionts in stony corals if surfacial water temperatures increase beyond some 33 °C.

Of course, the ocean can also be considered a photochemical reactor at and near to its surface, with additional inputs by photosynthesis. Chemical elements respond to changes of conditions with changes of speciation and other reactions inducing establishment of yet novel equilibria. Speciation studies at ultratrace (picomolar and even below) concentrations, now feasible for some 30 years—allow us to understand both the sequence and the outcome of corresponding chemical transformations. This allows for additional statements concerning bioavailability of chemical elements in “natural” and perturbed (by some pollution) marine environments.

It turns out from studies of redox speciation of both metals (Cr, Fe, V, Ce) and non-metals (N, As, I, Se, Te) that conditions get close to the equilibrium state given by local redox potentials, or, conversely, the latter can be calculated from pH being 8.3 and the distribution among different redox states (for data, e.g., Nozaki, 1997). Taking the concentration ratios, say, iodide/iodate, and listed Eh values it is feasible to calculate an effective redox potential for any of these redox couples, with

38) Inside of organisms (leaves, needles of green plants), Eu (Eu^{3+}) apparently also undergoes photochemical reductions as evidenced from its fractionation behavior which is quite untypical for rare earth elements but similar to that of heavy alkaline earths (Fränzle 2010).

39) In earlier decades, acidification of ocean waters was sometimes and somewhere

induced by discharges of acid solutions produced in making titania, now it happens on a global scale and going to get more so if liquid carbon dioxide is deposited in deep-sea areas to remove it from the atmosphere after combustion processes were done.

Table 2.6 Concentrations and amount ratios of different oxidation states of certain elements in ocean water (middle/western Pacific Ocean). Column six gives the standard redox potential while the rightmost column seven has the value valid for pH 8.3 and the given concentration ratio (column four).

Element	Oxidation state	Concentration (ng/kg)	Ratio (oxidized/reduced form)	Log _{ratio}	ϵ_0 (V)	$\epsilon_{\text{eff. (pH 8.3)}}$ (V)
chromium	+ III	2	105	2.02	1.350	0.58
	+ VI	210				
arsenic	+ III	5.2	230	2.37	0.560	0.23
	+ V	1200				
selenium	+ IV	55	1.8	0.26	1.15	0.68
	+ VI	100				
tellurium	+ IV	0.02	2.5	0.40	1.02	0.55
	+ VI	0.05				
iodine	–I	4.4	13 000	4.11	1.085	0.85
	+ V	58 000				

the values nicely agreeing except for arsenic⁴⁰⁾ (the value for Te is insecure, given a comparison among older data in the femtomolar conc. range). Cr(VI), chromate, undergoes rapid photoreduction⁴¹⁾ with dissolved organic nitrogen (DON) including amino acids or humic matter; accordingly the calculated value ($E = 0.58$ V) is likely to be too small also. Exact data are given in Table 2.6.

Accordingly at least for oxygenated although photochemically biased samples from northwest pacific it is obvious that these elements are (fairly) close to redox equilibration compositions. Enzymes which catalyze redox processes at metal ions or nitrate, nitrite use to contain and employ molybdenum and also operate on “non-physiological” redox-active substrates like As, U, I, Cl (both chlorate and perchlorate, each affording chlorite ClO_2^-). These Mo-dependent oxidoreductases thus are hardly selective but exactly therefore producing “sound” close to equilibrium states. If so, one can use Pourbaix diagrams straightforwardly to estimate or predict the speciation of these and yet other elements in marine conditions, just by looking up the corresponding stable form at pH 8.3, $E_h = 0.65\text{--}0.70$ V in the respective diagram. In well-oxygenated freshwaters, even higher potentials of more than +0.9 V are seen, partly due to lower pH.

Comparing this to the above table, it becomes evident that shares of oxidized states of the five elements can hardly be increased much further than in the ocean.

40) As(III) concentrations might be reduced by its being the substrate of biomethylation (which rapidly occurs with As and is most common in marine organisms, whereas As(V), being just 50-times less abundant than “reactive phosphate”, is going to be involved in precipitation of inorganic binding forms. Accordingly, the redox potential calculated from data for arsenic

may be biased either way (positive or negative).

41) Redox equilibria involving Cr or As are established by Mn oxide colloids acting as redox catalysts. MnO_2 particles do exist in seawater but are sensitive to photoreduction themselves, possibly impeding establishment of other elements’ redox equilibria in aerated waters.

Matters are different with Ce and V (vanadium being an essential ultra-trace element for animals and fungi), with a profound effect on solubilities.

2.2.2.5 Non-Equilibria among Different Water Layers Can Promote Chemistry, Biological Processes and Deposition of Materials

Non-equilibration states with similar ramifications like those observed in air also occur in water, due to both transport and of biological activities (which partly removes such non-equilibria, for example, present with NO_3^- and H_2S coexisting, by drawing chemical energy out of them), including:

- River estuaries (pH and salt concentration “jumps” between river and ocean waters);
- In wells and springs, providing contact between air oxygen and reducing water solutes (H_2S or Fe^{2+}), with iron-oxidizing bacteria making their metabolic energy (proton transport-coupled phosphorylation) by letting O_2 react with Fe^{2+} ;
- At hot springs in the deep sea, which grossly differ from their otherwise highly homogeneous environs both thermally and chemically;
- Halo- and thermoclines, which block mixing of different water layers seasonally or even completely, producing a discontinuity in redox potential when this gradient exists sufficiently long to deplete dissolved oxygen and nitrate below some mixing barrier (often, some weeks will do);
- Due to biological activity (if eutrophication causes mass growth of algae and thus oxygen oversaturation close to the water surface combined with transport of large amounts of reducing organic matter to deeper layers).

Such non-equilibrium conditions and sites then provide momentum (free energy) for chemical and related⁴²⁾ processes. All the sites mentioned in the above list offer chemical potential differences useful to start reactions which either deposit solids—for example, heavy metal sulfides in black smokers—or be used by chemolithoautotrophic organisms (in an indirect manner via phosphorylation rather than directly employing reductants like CO , H_2 , SH^- or Fe^{2+} to reduce CO_2 or some adduct thereof directly). The range of chemolithoautotrophs includes, for example, iron bacteria in springs in Central Europe as well as sulfate reducers in “oases” next to middle ocean ridges. Either way, these organisms become primary producers and thus the backbone of trophic chains where there is no light for photosynthesis (deep ocean, caves). Just by features and products of their “exotic” modes of metabolism, they are capable of also enriching potential pollutants considerably:

42) After decades of corresponding microscale experiments which aimed to make use of osmotic energy at estuaries, namely the ion concentration differences between fresh- and ocean waters, a small power plant (3–5 kW electrical output) has actually been built and connected to local grid in Norway quite recently. At

semipermeable membranes salt concentration differences give rise to a mechanical pressure difference which can either translate into some electrical diffusion potential or be used directly to “pump” water upwards and then exploit the potential energy in classical running water power plant manners.

H_2S production by SO_4^{2-} reduction in cold waters will in turn precipitate and pile up toxic elements such as cadmium, mercury, lead, arsenic and antimony in the formed or ambient sediments, simply because all their sulfides are extremely hardly soluble. When such sediments are exposed to oxygen later (e.g., during mining), these element sulfides undergo oxidation once again, causing an often massive leaching and input of these elements.

2.2.2.6 Biogeochemical Cycles in Water, Stoichiometric Ecology and the Design of Sewage Treatment Plants Making Use of Biotechnology

Except for plankton algae, living organisms have the composition of the main elements set by genetics to keep it constant even against environmental challenges. Thus an excess of some principal element besides C—that is, either N, P, or S—is going to be excreted if the supply does not match the amount of consumable carbon. Now, it is quite common in sewage treatment biotechnology: (i) to use consortia of living organisms to consume organic fractions and odd-N compounds in the sewage and (ii) to expose these consortia to mixtures of the four elements C, N, P and S whereas the ratios of which vary with time erratically. Given the above rule of ecological stoichiometry, it follows that a given consortium of organisms will either change its internal composition, up to extinctions of some species involved, and give away to above excess(es) of some element(s) to be finally discarded into the next river. On the way to reducing TOC and odd-N levels to acceptable levels, organic and inorganic pollutants such as C, N, P compounds and metal ions either turn up in the produced biomass (i.e., sewage sludge) or get into the gas phase as CO_2 , CH_4 , N_2 . Either way, there is no reason to assume that the supply (composition of sewage water) ever matches the demands of the organisms involved (+ some C excess to be oxidized into CO_2), demands the relations of which are fixed by genetics, after all. Something will thus make its way through all the system stages inevitably, and the more so, if the mismatch causes some organisms vital to functioning, for example, those which accomplish denitrification, to get extinct from this sewage treatment plant.

Consumers which have C/N/P ratios grossly different from those of their favorite prey, are forced to consume more although incompletely, and to oxidize more of the absorbed C compounds, hence can be expected to be more agile. Constraints by ecological stoichiometry have many drawbacks in environmental engineering, all over applications of biotechnology as well as in agriculture: sewage treatment plants were discussed before, which effect removal of C [all total organic carbon (TOC), chemical oxygen demand (COD) and biological oxygen demand (BOD) values must be considered], N and P from water by means of complete trophic networks (keep in mind that feedback of sewage sludge as a nutrient for denitrifying bacteria translates into the sludge organisms, with their C, N and P contents being consumed by other microbes!). Here, like in processes such as biological desulfurization of fossil fuels, the composition of sewage water solutes in terms of C, N, P should (except for some C excess) match that of the involved microorganisms to achieve meaningful purification results. Otherwise, either organic C has to be added (feeding of, e.g., methanol) or P is going to be artificially

precipitated by adding Al(III) or Fe(III) salts; N cannot be removed by precipitation because there are no insoluble nitrates, while $\text{Mg}(\text{NH}_4)\text{PO}_4$ readily falls ahead of nitrification (NH_4 oxidation to NO_3^-) if sufficient Mg^{2+} is available.

The situation is somewhat different if one strives for either S retention in bio-filters or cleavage of sulfur from fine-milled lignite or crude oil: here, C/S and N/S ratios do matter while in the latter case, converting dibenzothiophene and other compounds, C/S of applied organisms should be far smaller than in the substrate (which may contain several percent of sulfur!) because one wants to maintain most of the carbon for combustion and energy conversion purposes. With C/S (stoichiometric) ≈ 100 in sulfur-rich coals or about 500 in common crudes, this tells us the organisms applied for this way of desulfurization must be considerably more sulfur-rich than usual (C/S = 400–700) which, however, is sometimes observed⁴³⁾ in pertinent microorganisms, or excrete S to an aqueous leaching phase efficiently. Oxidized sulfur is leached by water (washing of granulate, oil phase) as either sulfite or sulfate. In sulfate reducers, C/N/P is much higher than the colloquial Redfield ratio of C/N/P = 106:16:1; namely, about 700:6:1. The treated product is still usable as a fossil energy source, however, biomass must also be extracted as it contains much of N and S producing unwanted products (HCN, NO_x , SO_2) if co-combusted.

Water-soluble and particle-forming contaminants which get into a sewage treatment plant are mainly biological in origins, with organic compounds dominating, besides fecal components and tensides from soap, washing, dish-washing and laundry detergents, but—alas—lots of substances which “should not be” present in wastewater, are also funneled into sewers illegally, like the remains of colors, solvents or salts and macroscopic waste items. In addition, rainwater in industrialized countries did take up so many atmospheric pollutants in air and then by run-off over roofs and the like that it has to be treated as part of domestic wastewater in sewage plants after being directed to sewers from private grounds (yet, it is not illegal and people are also encouraged to use it in exchange for potable water from the tap for certain purposes, including irrigation, laundry, washing, showering and WC use in Germany and other EU countries). Snow is much more highly polluted, especially taking up aerial acids. The resulting mixture which gets into the sewer of course can be analyzed and its composition is going to vary with time (which is of no much practical use for sewage treatment plants as they have to deal with all the stuff anyway regardless of variable compositions, but they can be informed if there are contaminants which directly hit and compromise the bioecosis involved in sewage treatment, like silver salts, or would pass to the river

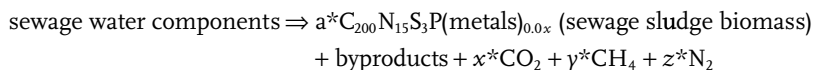
43) Ferredoxines, also involved in S reductions and partially also oxidations, are FeS clusters, and a local sample of iron(II)-oxidizing aerobic bacteria was found to contain more S than N (C/S = 16.7; C/N = 22). For *thiobacillus ferrooxidans*, elemental sulfur is oxidized to SO_3^{2-} by-producing Fe^{2+} by electron transfer to

Fe(III) (Sugio *et al.* 1987) in a ferric oxidoreductase. *T. ferrooxidans* is most used for purposes of biological desulfurization, also converting organic S, sulfide and pyrite or marcasite. Sulfur oxidation here requires glutathione.

without being chemically changed in sewage treatment). The subsequent procedures will change the elemental composition in a stepwise manner:

- *Nitrogen* [as urea, N organics (DON), NH_4^+ , etc.] will be first oxidized to nitrate (nitrification) and then reduced into N_2 (denitrification), the latter escaping from the open sewage treatment basins into the atmosphere;
- Parts of *carbon* will be oxidized to CO_2 , another will escape as biogenic natural gas (CH_4) from the fouling part (splitting dissolved acetate into the two gases CO_2 and CH_4 will thoroughly reduce residual TOC and COD by removing C to the atmosphere or rather, to controlled, energy-producing combustion⁴⁴);
- *Phosphate* is precipitated in two different phases of sewage water treatment, first using $\text{Ca}(\text{OH})_2$ to produce hydroxyapatite, finally residues by $\text{Fe}(\text{III})$ - or Al salts just before discharging; neither process is biotechnological;
- *Biomass* is produced (sewage sludge), of course containing C, N, P, S and many metals in a ratio typical for the pertinent sludge organisms; protozoa then devour parts of these. Thereby, some part of C is oxidized into CO_2 and vented while N and P will often undergo re-mobilization;
- Upon *fouling* sulfate hitherto dissolved is reduced; sulfide in addition can be formed from S organics in sludges processed in the tank. Changes of ratios of sulfur vs. other elements can be either positive (relative S increase due to C venting) or negative (precipitation);
- *Heavy metals* are going then to be precipitated as sulfides in fouled sludge, after parts of them were removed before in $\text{Ca}(\text{OH})_2$ treatment.

The original ratio C/N/P/metals in untreated sewage waters will hardly match that of either sewage sludge or the biological fraction of the latter, fouled sludge and so on. The purpose of this is to remove carbon—TOC or CSB or BSB alike—from the liquid and biota associated to it by venting like happens to nitrogen upon denitrification. Reduced C continues to prevail—as can be seen from the large combustion energy of dry sewage sludge, which is close to that of lignite—but both ratios C/P and N/P will decrease. This process can be summarized in a simplified reaction equation. It takes account of all well-defined simple kinds of biomolecules, the gross composition of biopolymers and the analytical data on sewage sludge:



If there is not sufficient C or N to fully incorporate P into sewage sludge biomass as ATP or nucleic acids⁴⁵, P and possibly also S will turn up in the (partly soluble)

44) Venting methane would not only mean spilling an energy source and a potent greenhouse gas, causing explosion hazards, but would also release byproducts which can be highly dangerous in landfills and also sewage treatment.

45) As a rule, small C/P and N/P ratios, that is, lots of phosphorus, directly translate into high metabolic activities (ATP!) and/or reproduction rates, especially in bacteria (Sternier and Elser, 2002).

byproducts. While this does not matter so much with sulfate, phosphate brings about a risk of eutrophication; the same holds for N after denitrification remains uncompleted to leave after dissolved NO_3^- or possibly (after fouling) reduced odd-N species. There are different groups of heavy metals considering their behaviors in sewage sludge depending on other (non-metal) components: while Cd, Co, Cr, Ni, and Pb are deposited in sludge regardless of its N and P contents, levels of Cu increase along organic N content (Bellehumeur *et al.*, 1997). Probably Cu will coordinate to both amino acids and larger N-containing molecules (forming hardly soluble coordination polymers in either case), while other metals form less stable complexes with neutral or anionic N donors and thus get precipitated without interacting with either N or P compounds. Metal contents in sludge do but weakly correlate to those of untreated sewage water (Bellehumeur *et al.*, 1997), suggesting the actual contents rather correspond to biological (enzyme) heavy metal demands of organisms which live in and mostly constitute the sludge. It is intriguing that there is so much molybdenum (12.6 mg/kg dry matter; Krogmann *et al.*, 1999), which is probably related to the eminent role of Mo in nitrate reduction (nitrate reductase) in both bacteria and plants (Bernhardt, 2011); possibly the same holds for Cu effecting the further steps of N reduction. However, it must be noted that both essential and non-essential elements (e.g., Cd, Cr) pile up in sewage sludge.

Metals usually do not get into the gas phase, neither does phosphorus in common (acceptable) parameters for running a sewage treatment plant: while both archaea and clostridia can reduce phosphate all the way to phosphane PH_3 (Thayer, 1995), this takes very low redox potentials, and biomethylations of As, Sb or metals such as Sn, Hg, Pb is also avoided in any stage of such a plant.

If ratios C/P or N/P still do not match those of sludge after treatment, additional measures for precipitation must be taken (see above) or the system must be adjusted by introduction of additional reduced carbon. In sewage treatment protocols, either some part of the biomass grown inside the system is used as food for other bacteria (sewage sludge feedback) or methanol, molasses and so on are added. The approach and reasoning of ecological stoichiometry enable to analyze operating conditions and achievable completeness of yet other biotechnology-based purification or transformation procedures in quite the same way.

2.2.3

Soils and Sediments

All organisms in active life (rather than anhydrobiotic dormant states and preserved seeds) are directly linked to water spatially, and aerobic organisms are also to air, whereas most organisms are linked to soil, sediments and ground water in a rather indirect spatial relationship only unless, of course, being terrestrial plants or fungi. In appropriate reactor vessels water bodies respond to changes of pH or redox potential by chemical or biochemical/biota changes, and likewise water does when running or trickling downward through different soil horizons. Thus soil horizons can be used in much the way to purify percolating water introduced at carefully chosen sites like when the water would be passed through the

subsequent stages of a sewage treatment system. Such soil-chemistry-based water purification systems are called sewage farms (fields to be irrigated with sewage) or, if purposely covered by plants, planted soil–water filtration units (in German: “Pflanzenkläranlage”).

A typical horizon stratification of an evolved soil is depicted in Figure 2.11. This stratification allows to purify water by having it pass layers with different chemical properties, particularly different redox potentials and pH, eH values, contents and compositions of organic substances. Of course, kinetics also are an issue: as a rule, excess nitrate will make it through more reducing, anoxic soil layers rather than be reduced to N_2 or ammonium ion as: (i) denitrifying bacteria are very scarce there at best and (ii) abiotic reductions of NO_3^- [possible reactants from a thermodynamic point of view: e.g., Fe(II), sulfide or various organics including phenols] are kinetically very slow except for very low (i.e., nitric acid) or very high (thus alkaline components are non-existent in soils) pH values [e.g., $Fe(NO_3)_2$ is a quite stable crystalline hydrated salt which can be substantially heated without undergoing internal redox decomposition to produce NO_x and magnetite or $FeO(OH)$].

Hence, components dissolved in the water to be passed through the soil layers are poised to get adsorbed, precipitated, undergo redox processes or become part of biomass at one site or another, depending on local conditions. The same holds, of course, likewise with polluted rainwaters or after inundations of river shores and more remote sites. In turn, if an ongoing coverage of the soil–air interface by acid rain, sewage waters or even sewage sludge alters the chemical properties of the uppermost soil layers, sooner or later the underneath soil horizons will also respond by changing their properties. Sometimes, these will take about as long as soil stratification (about a century), but the simple fact that there are no nitrates which are insoluble in water (or similar solvents) will cause this rather strong oxidant to get into hitherto reducing soil decks rapidly if water is steadily put to the surface in excess of local evaporation. As mentioned before, it takes peculiar chemical or biochemical conditions to have it undergo rapid reduction in groundwater, otherwise it will make its way right down to the next subterranean aquifer. However, both chemolithoautotrophic soil bacteria and deep-rooting land plants are influenced in their living conditions and also element uptake by changes of both redox potential and gas compositions caused by a nitrate burden in the soil. Accordingly, effects may proceed through trophic chains, apart from eutrophication of waters which results if the nitrate gets back to the surface in springs fed by polluted groundwaters.

2.2.3.1 Soil as a Multiphase System

In pedology (soil science) quite simple tests are used to get an idea about some soil on site, without lengthy and apparatus-demanding analyses. These simple tests suffice to prove that soil is a complex system, by wetting it, then trying to knead it, form and bend small rolls out of moistened soil, or to look for suspended particles which were washed out. The principal components of soil, namely, sand/gravel, humic matter and clays, loam can be identified in this manner and even their shares can be estimated. Hence, soil is:

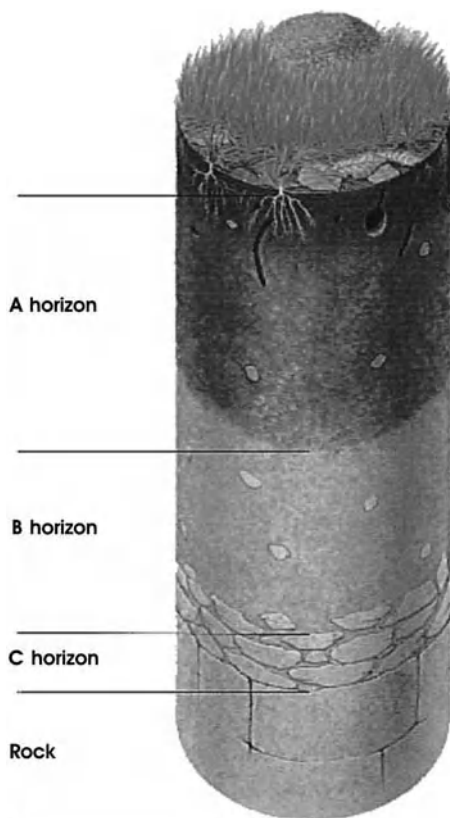


Figure 2.11 Typical stratification of soil layers. A horizons are mineral horizons in upper soil layers (next to leaf litter, grasses) in which humic matter does accumulate, dyeing it brownish to black. The adjacent (next bottom) B horizon likewise is a mineral horizon but with chemical changes of the mineral inventory due to both weathering and washout additions from topsoil. As humic matter levels are lower than in A horizons, partly due to the metabolism of earthworms, its color differs from those of both A horizon and bedrock (left and right pictures), even if brightly colored metal oxides like iron pan happen to form there. Eventually, the lowermost C horizon is a mixture of loosely scattered pebbles and fine-grained soil which

often is rich in lime and thus coherent enough to be dug out as a compact sample. While humic compounds in A horizons act as polymeric ligands*, the redox potential starts to decrease between A and B. The B horizons often are solidified by inclusion of iron oxides forming there from Fe^{2+} transported upward with groundwater and dioxygen diffusing down along root channels. These Fe(III) oxide phases effectively retain such anions which form insoluble Fe(III) salts (phosphate, phenolates). Ca^{2+} acts likewise on anions strongly interacting with calcium down in the C horizon, in addition the alkaline pH of this horizon further reduces mobilities of heavy metals except Zn. Photo: © Wissen Media Verlag, Gütersloh/München, Germany.

* Concerning plant-root resorption of metals, polymeric humic matter does indeed complexate and thus extract to water various heavy metal ions from sulfides and other speciation forms in sediment, the produced complexes are polymeric and hence so bulky

that they effectively cannot be resorbed by plant roots. Accordingly, additions of humic acid to some hydroponic culture will cause *reduced* uptake of those metals which form particularly stable heavy metal complexes.

- A mixture of various solid phases which differ on both their properties and their shares vastly. In addition, there are:
- Groundwater occluded among the single soil particles, plus:
- Air or other gases due to biochemical production.

As a rule, there is less O_2 , more CO_2 and water vapor than in the “free” atmosphere, plus small amounts of methane (CH_4), N_2O , CO , H_2S and in carbonatic soils also NH_3 , which all escape to the atmosphere slowly but steadily (Scheffer *et al.*, 2002).

If the soil has been compressed or completely wettened, the gas (air) phase is missing, thus there is no more O_2 available to local soil organisms. For oxidizing organic matter in their metabolisms, both to process it and obtain metabolic energy (ATP), the soil biota then must make use of less powerful oxidants than O_2 , as a rule first taking the strongest one which is still available (which then would be nitrate), only then resorting to even lesser oxidants like Fe or Mn oxides, arsenate, sulfate and so on. The same will happen if some other gases, like methane from either defective natural gas pipelines or biological production, leak into topsoil and thus replace air (often trees die in cities at streets when natural gas pipelines get defective somewhere under the sidewalk or else almost complete coverage of soil by stones or asphalt stops air getting into soil also). With water missing, certain phases are no longer stable, with clay minerals subject to irreversible drying processes, or cannot be replenished anymore: a dry soil will no more sustain a kind of biomass which via ongoing decomposition of litter gives rise to new humus, in addition losing that which is already present by erosion, with the risk of desertification. Whereas both liquid and gaseous phases can be thought to lack or be replaced in soils, although at the expense of soil functions, the solid phase(s) cannot be eliminated – otherwise the soil or aquatic sediment simply stops to be a “soil” – even though in the above aquatic (limnetic) sediments their upper edge can become so fleeting that it can neither be precisely determined nor sampled without certain tricks (cryosampling, freezing the sample column *in situ* before removing it).

Liquid, solid and gas phases within soils thus depend on each other concerning both long-term existence and biological functions as well as those derived from the latter in, for example, agriculture and forestry. A productive soil must include all three phases in sufficient extents and qualities. Table 2.7 gives the shares in soils next to the surface, by volume.

These largely differing densities end up to give an average soil density of some 2 g/cm^3 . Of course, as already implied by the above considerations and facts, all three phases (soil air, ground- and hardly mobile crystal waters, various solid components) are also involved in chemical reactions which alter soils by time⁴⁶⁾.

46) When air gets into contact with Fe^{2+} - or Mn^{2+} -rich ground waters in sandy soils, the oxides Fe_2O_3 or MnO_2 will form and firmly connect the single sand grains to produce first iron pan and eventually sand stones. When acidic (H_2SO_4 -bearing) rainwater

penetrates calcite (lime)-rich soils, gypsum will be formed which likewise can “glue” together particles of various sizes including gravel to each other. In either case, water permeability will decrease.

Table 2.7 Average composition of soils, revealing volume shares and average densities of the distinct phases.

Fraction/phase	Volume share (%)	Density (g/cm ³)
Air (<i>a</i>)	5–40	0.001
Water (<i>w</i>)	15–30	1.0
Mineral components, sand	$[100 - (a + w + o)]$	2.6–3.0 ^{a)}
Solid organic matter (<i>o</i>)	ca. 5–7	1.0–1.2

a) Some mineral phases which occur in soils, for example, Fe_2O_3 , have far larger densities (in this case, 5.25 g/cm³).

These shall be considered in their context and interaction, hence: soil air, ground water, and solid phases also differ in other parameters and properties besides density and chemical composition and accordingly are also involved in soil functions and properties to be discussed below. Often, like with ion exchanger properties, several of these sub-phases of soil interact to produce the observed behavior.

2.2.3.2 Important Chemical Features of Soils

Soils behave as:

- Ion exchangers;
- Buffer systems;
- Reducing agents;
- Reservoirs for water and a manifold of mineral species. These reservoirs are tapped by springs and plants alike, transporting some dissolved items out of the soil.

Whereas transport speeds of groundwater—both horizontally and vertically—use to be of the order of some m/year, the ion exchange capability of soil serves to control and delay transport of both cat- and anions which got to the soil with rainwater, aerosols, dust and so on. Here, the transport rates of ions are no longer dictated by the flow speed of groundwater (or by mere adsorption) but depends on which cat- and anions are present in a solid, immobile soil phase, which other ions “compete⁴⁷⁾” for exchange at anchor groups in the soil liquid and which functional groups of either charge sign exist there to which ions can

47) Examples: cesium ions (¹³⁷Cs, other radiocesium isotopes now extinct) from Chernobyl aftermath were transported to depths of 50 cm up to 4 m depending on kind of soil. Protons from acid rain or—worse—snowmelt will remove (elute,

technically speaking) the essential plant nutrients Mg^{2+} or Ca^{2+} from those levels of soil where they can be absorbed by roots. This cannot be compensated by the fact that the same holds for some toxic dications, for example, of Pb or Cd.

become attached electrostatically for some time, that is, reversibly. The ion exchanger function mainly is due to partly decomposed (oxidized) polymeric organic substances.

Buffer activity requires the presence of agents which can both take up and release protons, like anions such as $\text{CO}_3^{2-}/\text{HCO}_3^-$ in soil minerals but also by clays and phosphate minerals such as hydroxyapatite, certain organics like pectin and so on. Clays both contain water and Al^{3+} embedded in a silicate matrix. Here Al^{3+} acts as an acid and the silicates can absorb protons (base), permitting to deal with impacts of either acids or bases (carbonate dust aerosols, ammonia gas being absorbed by the soil at areas of intense manure) to some extent without thorough changes in pH of soil liquid. Soil liming is hence undertaken to bind acids and re-supply the soil with Ca but also brings about degradation of humic matter and release of odd nitrogen. While the buffer function of soil is amended the ion exchanger properties get somewhat compromised.

Common reductants which also provide metabolic energy if devoured by some (heterotrophic) organism, include organic matter, for example, phenol functions of humics (which are degraded, e.g., by earthworms), sulfide ion, or Fe^{2+} .

Springs contribute to leaching of substances which may be involved in constructing and maintaining the above soil functions, as does erosion. As a result, at least an aquifer and nearby layers may be depleted in such substances, decreasing stability and resilience of soil toward the above kinds of chemical challenges. In agriculture, a key purpose of adding fertilizers is to avoid destabilizing and compromising soil chemistry which otherwise would result from taking away plants which before extracted corresponding substances from the soil.

The character and extent of reservoir features sensitively depends on local soil chemistry, as does the chance/risk to elute pertinent ions.

2.2.3.3 Soil as a Bioreactor

A bioreactor is a system the chemical activity of which is shaped and dominated by the organisms which dwell in it, rather than by inorganic, “plainly” organic, even catalytic entities. Such prevalence of biochemistry is neither seen in air nor in the vast majority of natural waters [when air or water are biologically cleaned by passing them through some moistened porous matrix (“biowasher”) containing “adapted” bacteria to degrade organic pollutants, this translates into the biochemistry occurring in some kind of soil—though highly contrived, artificial and atypical]. Soils are different indeed, simply due to the fact that: (i) there are lots of organisms of quite different sizes and metabolic pathways in soils and (ii) of (now) non-living organic materials (often, 5–10%). Accordingly, soil is the only environmental compartment chemistry in which is dominated by biological activity and hence soil itself can be called and considered a bioreactor of its own.

Soil is all precondition, substrate and product of biological activities: while higher plants resorb substances out of it, in turn its organic fraction is amended by decay products of them, including leaf or needle litter, including some which

are hardly degradable by microbes (lignin, polyphenols from needle litter⁴⁸). Many organisms either feed on (some fraction of organic) soil substance directly or make use of it in energetic (catabolic metabolism, like fungi or iron-oxidizing bacteria. Every humble compost heap can give an idea of the rate in which organic plant litter is converted into something morphologically and chemically similar to (A horizon) soil when conditions are optimal; the normal timescale to do this conversion ranges from years to decades, however. Of course, kinetics of feedback of different fractions generally depend on reactivities of the corresponding kinds of compounds and accessibility of their key functional groups to turnover by enzymes and, more rarely, by inorganic catalysts present in soil mineral fractions. The usual scale of relative kinetics is shown in Figure 2.12.

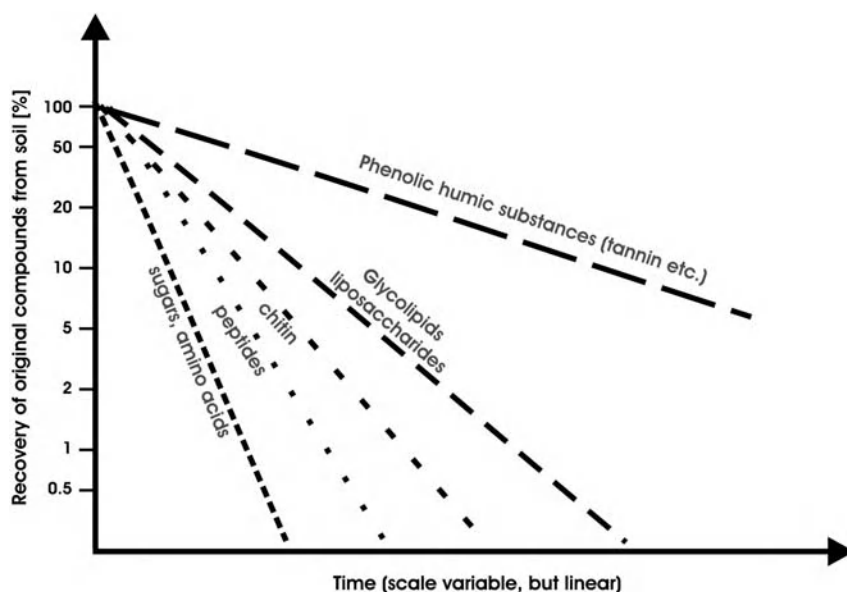


Figure 2.12 Relative degradation kinetics of various soil organic compounds. Log-linear lines imply the assumption of first-order chemical kinetics which is given in both a polymer being stepwise degraded and an enzyme operating at limiting conditions. Hydrolases in litter and soil also attack

proteins, producing peptide fragments or single amino acids which means that binding by AA side chains will be replaced by the usual N,O-chelation of aminocarboxylates. Modified after Bardgett (2005), using additional data from Gleixner *et al.* (2001).

48) Here metazoans take over: earthworms degrade polyphenols while basidio- and some ascomycete fungi are the only organisms which ever “learned” how to attack lignin—by means of manganese exoperoxidases. While wood contains

usually small amounts of metals, earthworms then have to deal with the residues also of electrophilic organics which did accumulate in humic matters earlier, like with As, Sb and heavy metals.

Here, just removal of the original compounds is considered which need not include or imply cleavage of the functional groups binding metals; for example, during saponification of the phospholipids which are highly abundant in fresh litter and young soil materials *a*- or monolipidated glycerol phosphates are produced which have rather identical complexation properties. The time scale of degradation is linear but will depend on climate, humidity, . . . As a rule, lifetimes of sugars in temperate-climate soils are in the order of weeks to months

As a result, soil is much more shaped and altered by various kinds of biological activity than either of the other environmental compartments; moreover, the shares of both living and dead biomass exceeds those in water by far [a (typical) BSB value of some 10 mg/l in water corresponds to some 7.5 mg C_{org} /l, as compared to an average glowing loss of 4% in common soils; i.e., 40 g/kg dry matter or some 70 g/l in common humic upper soils; i.e., a difference of four powers of ten as compared to C_{org} in water].

Microbiota and plants which grow at the surface do interact: plant roots (and fungal mycelia) do deliver and give away chelating agents like malic, citric, hydroxamic⁴⁹⁾ and some amino acids, then binding to metal ions in the soil to dissolve and coordinate mineral components of the solid soil fractions. The larger part (60–70%) of these organic ligands is never retrieved by the plants (Bardgett, 2005) but rather consumed by microorganisms in soil, thus feeding heterotrophic bacteria and of course enhancing their supply of metal ions which they also need (see above) while the microorganisms accomplish partial oxidations of polymeric organic matter (particularly, of cellulose) which introduce carboxylic (and to some extent phenolic) groups which only bring about “soft” (slightly acidic pH) ion exchanger properties of soil. These almost symbiotic cooperation modes among organisms rather different in taxonomic terms also involve fungi: mykorrhiza shuttles also organic matter between different plants, besides of metal ions.

2.2.3.4 Gradients Do Form in Soils

Soil itself is not mobile, except for local landslides, and flow speeds of groundwater and soil-occluded air are slower than those in rivers and open winds by many orders of magnitude. Hence chemical state differences among fluid phases at different site of some soil will not readily be compensated as diffusion of possible reaction partners is impeded and hence very slow. Photochemical impacts to shift a corresponding equilibrium are limited to some uppermost millimeters in soils. Chemical species which are not compatible to co-exist according to chemical thermodynamics (which can be seen when, e.g., superposing Pourbaix diagrams) will thus keep on to exist in soil when just a few centimeters apart as the low mobilities of all the partial phases of soil—gaseous, solid, and liquid alike—prevent mixing

49) Formally speaking, hydroxamic acids, prepared by splitting ester linkages by hydroxyl amine NH_2OH or its derivatives $R-N(OH)-H$, are oxime derivatives of carboxylic acids, replacing $R-\{C=O\}-(OH)$ with a $R-\{C=N[OH]\}-OH$ moiety. Both the

C- and N-bound hydroxy groups act as acids, making hydroxamates bidentate ligands which bind to metal ions via both O functions (not the N atom!). Being chelators, their complexes use to be more stable than carboxylatocomplexes.

and thus reaction quite efficiently. Moreover, the time it takes to cover some distance by diffusion increases with the square of the distance, making oxidants which come from above (air dioxygen, dissolved nitrate, etc.) get deeper fairly slowly. Accordingly, they will soon undergo consumption by local organic matter and organisms; below that level only weaker oxidants such as sulfate or Fe(III) will persist, if at all. Hence (mainly vertical) gradients of redox potential and other terms form which in turn alter stratification of soil by the very chemical reactions they bring about secondarily: this kind of feedback causes the gradients either to become steeper or less pronounced with time until some diffusion equilibrium-related state is established. However the latter may be subject to perturbations, for example, soil compression, surface flooding, -covering or -plowing to change entrance condition for O_2 , fertilizer applications combined with stronger rain washing NO_3^- to deeper layers and so on.

As mentioned before, strong oxidants use to be available at the upper edge of a terrestrial sediment; besides O_2 from air there is some locally produced by photosynthesis in vegetation next to the surface (e.g., grass). Deeper layers of soil are distinguished by dissolved mineral salts some of which are reductants, like Fe^{2+} , as are many of the plentiful organic compounds. In forming the redox gradient, parts of soil are “sandwiched” among oxidants from above and reducing agents from below. What happens now at a given site depends on the dominating direction of water (and gas) transport, with evaporation moving water upward, while trickling down after precipitation, snowmelt, irrigation cause a downward flow, eventually down to the next aquifer or some saturated layer. If there is a barrier, formed say, by clays, iron pan, or loam, the water will flow almost horizontally until re-surfacing in some spring. Though stationary, or rather because they are stationary, soils display gradients in both redox potential and moisture levels, with the latter plus evaporation controlling vertical transport of redox-active agents.

However, there also are mobile bodies of soil, such as migrating sand dunes and moraines (Figure 2.13). Exactly due to this transport process, there are small – if any – shares of organic matter which defines soil⁵⁰⁾ in chemical and pedological senses of this word. Moraines, as being produced by glacier ablation of bedrock, even contain lots of coarse matter. A migrating dune, for example, the huge dunes of Courland Spit in Lithuania and Kaliningradskaya Oblast (Russia), keeps migrating over long periods of time exactly because there are neither organic matter nor dissolved metal ions inside to solidify it and moreover the dearth of organic substance, lack of ion exchanger capacity and a but minimal capability to retain water cause grave obstacles for plants to grow on it. Once plants would grow their roots

50) This is also why soil-analogous materials on other celestial bodies of the Solar System (see below) are not referred to as “soil” but rather as “regolith”, almost regardless of their particle/grain/gravel sizes. Sand- or dust-like samples from Venus or the Moon are completely void of organic material, and the same probably holds for Martian regolith next to the

surface. Concerning Titan, there is no coherent terminology as yet, with water ice (HCN, benzene, long-chain hydrocarbons) forming the solid phase while the liquid itself is organic (CH_4 , C_2H_6 , C_2H_2): this setting is too weird for pedologists apparently. Accordingly, there are migrating dunes very similar to those on Earth on both Mars and Titan.



Figure 2.13 Migrating dunes as *mobile* volumes of soil (or, rather, sand) now are an exception among very many stationary bodies of soil. If plants are kept from growing due to dryness (deserts) or salt inputs (coastal regions) or both (Namibia, Peru, solonchak soils near Lake Aral former sites), soil keeps mobile (unless for salt crusts stabilizing dunes also) and remains poor in humic matter, not undergoing internal solidification and stratification. In turn, this is a disadvan-

tage for plant cover to establish. Typically stratification of soils takes some 100–200 years, during which the soil must stay where it is right now. By contrast, a migrating dune covers hundreds of meters during this period, in addition to becoming fully mixed up internally several times. Thus neither chemical nor moisture gradients can be constructed or only persist herein (left photograph: courtesy of Adrian Diehl; right photograph: courtesy of Kirsten Hildebrandt).

would provide a network in the sand which eventually stops the movement of the dune even though the wind keeps on flowing.

2.2.3.5 Perturbations of Soil Development

As mentioned above, there are feedback processes during soil development, aging: solid phases which will only persist if both air and water are available next to the soil, undergo chemical changes themselves. During some decades or centuries stratification of soil is produced after its being newly deposited by water, wind or anthropogenic activity.

Soil strata produced and defined by chemical gradients before are perturbed all by digging animals (e.g., earthworms, moles, rabbits or badgers), downward diffusion of air along hollow root channels produced by rotting (dead) roots, and human activities (ploughs in agriculture) and by abiotic phenomena like erosion and formation of drought fissures. Rather than being the terminal result of a process once to be passed, stratification may be perturbed more or less regularly down to some 1 m at least. In addition there are chemicals in rainwater, like acids, photooxidants including H_2O_2 and nitric acid (both also present in unpolluted rainwater) and anthropogenic overlays like fertilizer applications and (formerly, outlawed in EU in 2003/2009⁵¹⁾) those of sewage sludge. In the latter case, toxic

51) EEC (European Economic Communities) directives 86/278/EEC (filed June 12th, 1986) and EC 219/2009 (filed 11 March 2009). Though neither stipulates that amendments by sewage sludge are completely banned, they pose the risk of

being held responsible for secondary effects to the peasant doing so in a way that it cannot be reasonably taken in economic terms—very much in the same manner like with discouraging the agrarian use of GOMs.

elements which accumulate by sulfide precipitation in digested sludge, including As, Cd and Hg, and excess amounts of others like Mo (with its antagonism to likewise essential Cu) will pile up on soil areas intended to be used in agriculture. Owing to these perturbations soil remains a dynamic system which permanently responds to its environment.

These responses (chemical reactions) are due to both inorganic solid phases— MnO_2 being most important as a redox catalyst⁵²⁾—and to biological activities (metabolism) in soil. If acidic precipitates do attack carbonates or clays, leaving behind just quartz sand or sulfates in the very end, there are acid–base (proton transfer) reactions, the same as if H_2S or elemental sulfur or sulfide minerals (pyrite, chalcopyrite) are oxidized biochemically to afford sulfuric acid. The outcome of this process is known as bacterial leaching: certain heavy metals, including some forming most insoluble sulfides, like Sn, Cu or U are mobilized and can be leached by water thereafter.

2.2.3.6 Implications for Soil Sanitation

Going to sanitize a polluted soil, there are two alternative options: either leave it where it is and do the necessary chemistry or washing on site (*in situ*) or remove it to some device where treatment can be done better or even in conditions one cannot create in a natural site (e.g., applying high temperatures, non-aqueous solvents, etc.—*ex situ*). In the latter case:

- The solid phase must be mobilized (dug out, mixed) before treating somewhere else or, during *in situ* treatments;
- Mobile phases of soil become the “carrier”/medium of the chemical influence or manipulation which achieves to purify (also) the solid soil phases. *In praxi* ground water is used for this purpose (Section 4.3.1), trying to purify or exchange soil gases only with very local pollutions.

Any transport process in an *ex situ* procedure is a grave intrusion into the soil system (keep in mind that its chemical properties and functions are mostly due to its very limited mobility!). For example, soil washing not just causes an extraction of pollutants but brings about an almost complete mixing of the former soil strata. Even when the soil is located at the original site again thereafter, it will take decades once again to reconstruct a quasi-natural stratification.

Generally speaking, there can be even more different kinds of contamination of soil than in either air or water, considering that soil pollutants can stick there also when being neither volatile or gaseous or soluble in water or readily adsorbed to particles but can remain in soil even having quite different properties (heavy crude oil, salts). If, however, the pollutant has one or another of these properties, removal

52) Cf. Section 3.2.2: if contacted with air dioxygen, aqueous Mn^{2+} or lower oxides like Mn_2O_3 , $\text{MnO}(\text{OH})$ [manganite] react to yield MnO_2 (birnessite, pyrolusite) at neutral or alkaline pH. In turn, pyrolusite acts as a catalyst for O transfer to and

oxidation of Cr(III), As(III), etc., to yield chromate or arsenate, respectively, massively increasing the rates of air oxidations of these two (and yet other) ions which otherwise would be very sluggish.

from soil *in situ* is facilitated, avoiding to relocate it: if pollutants are volatile or soluble in water, these can be decoupled from soil solids and treated like when purifying air or water, respectively. Evaporation can be accomplished:

- By heating the entire soil (classical addition of thermal energy);
- By located energy transfer into liquid phases (ground water) or p-type semi-conductors (iron pan) using microwaves (with the clystron located in some borehole)
- By dissolving of compounds alien to soil in water or other solvents can be effected by all water, organic or inorganic (liquid NH_3) solvents, supercritical fluids (most commonly CO_2) or tensides (inspired by petrochemistry, now obtaining most of the crude content of some *Lagerstätte* using non-ionic tensides).

Some solvents other than water or organics fulfill peculiar purposes in soil washing due to their specific chemical properties. Ammonia, liquefied by applying a pressure of some 6 bar at room temperature, becomes a powerful reductant besides an excellent solvent for both organics and quite a number of salts, once solvated electrons are distributed in NH_3 (or similar amines) by simply dissolving very base metals, practically sodium or calcium because these are the cheapest and non-toxic. Supercritical CO_2 is also used in de-cafeination of raw coffee, thus extracting fairly polar purines (and some components relevant for aroma of coffee) from it but serves the same purpose in separating crude oil hydrocarbons and phenols (both soluble in sc- CO_2) from humic matter and salts in soil treatment. In either case crucial components of soil—crucial for fulfilling the soil functions defined above—are maintained in the soil rather than eluted along the pollutants.

Soil also can bear macroscopic solid pollutants, from splinters of glass or pieces of wire up to car wrecks and the like. Of course such inclusions can be removed by some kind of sieving, but this inevitably destroys soil structure and stratification once again. Soil structure and stratification as spontaneously formed are crucial for maintaining the chemical soil functions.

Anyway soil washing and—even more so—methods of extracting pollutants by applications of compressed/liquified or supercritical gases imply removing soil from its original site, only finally putting it back to the “purified” site, if at all. The same holds for “harder” methods of thermal soil treatment, namely controlled pyrolysis⁵³⁾ and soil combustion. Soil combustion means burning the contaminants along with organic soil substance at $T \geq 1000^\circ\text{C}$, often using a natural gas auxiliary firing. Organics are fully oxidized in these conditions, and sand turns into glass whereas clays become ceramic matter, both glass and ceramic to include all the metals and their compounds which do not get vaporized in these conditions;

53) Controlled pyrolysis is also applied with analytic determination of organic C in soils, heating the pre-dried sample in air to $500\text{--}550^\circ\text{C}$ for a couple of hours. Then, organics are ignited and oxidized to CO_2

completely, while volatile metals and CO_2 bound in common carbonates remain in the site (except for forsterite MgCO_3 , dolomite and siderite FeCO_3).

toxic volatile elements include Zn, Cd, Hg, Pb, Tl, As and Sb⁵⁴). These are removed from the polluted soil (requiring to filter and treat the flue gases, of course) but also allows for an inclusion and lock-up of other contaminants by sinter, coupling and polymerization processes. Turning insoluble silicates, borates, or phosphates, into glasses by melting a precipitate also is considered and applied for the long-term lock-up of radioactive materials⁵⁵). Table 2.8 provides an overview of soil functions (ion exchanger, buffer, reductant and reservoir for water and other substances) along with the influences of various soil sanitation methods on these very functions, be it they make use of them or they change the capability of the treated soil to fulfill them (usually decreasing it permanently).

Although each *ex situ* method destroys soil structure, it is obviously not feasible to apply each imaginable method of soil cleaning *in situ*, instead. However, certain procedures are well-suited for *in situ* application or even imply it, namely:

- Washing, leaching and extractions using bacteria (bacterial leaching) for extracting heavy metal ions and degrading organic substances;
- Phytoremediation, trying to extract both inorganic and organic pollutants by vegetation planted for this very purpose, finally removing the resorbed pollutants simply by harvesting, and:
- Using reactive walls.

Often plants are used in phytoremediation (Section 4.2.1.3) which are so highly tolerant toward certain pollutants like Zn, Cd that no other plants are able to survive and thus compete on highly burdened sites {calamine flora (*calamine* = ZnCO_3), actually referring to various Zn minerals including silicates, or serpentine flora [growing on (Mg, Fe, Zn, Ni) silicates from weathered olivine, which woody plants cannot]}.

Hence sanitation should be achieved to remove or immobilize hazardous contaminants (e.g., by precipitation) without compromising the above soil functions. In optimal cases it is feasible to make use of them in purification procedures. An example of best practice is no-tensides soil washing/extraction using supercritical carbon dioxide in high-pressure vessels (at 200–300 bar),

- Ion exchanger function is not influenced because no tensides are applied in extraction;
- There is just small introduction of acids;

54) The same may happen during glass production: from the Middle ages, glassmakers in Rattenberg (Tyrol, Austria) made use of the flue gas condensate of raw sands as a rat poison, marketing it so effectively that eventually the entire town – now the smallest town in Austria – was named after this byproduct: the mountain (*Berg*) producing rat (*Ratten*)-poison (and casting deep shadows over the site)!

55) Here radioisotopes of Sr, Ba, Y, rare earth elements (La, Ce, Pm, Sm, Eu) from nuclear fissions of U or Pu are precipitated from nitric acid solutions by adding phosphate salts after fuel rods were used and dissolved, then turning the products into glass simply by firing them (cf. LaPO_4 -based glasses). Matters are quite similar in soil combustion although glassification of silicates and, sometimes borates, prevails over that of phosphates, then.

Table 2.8 The relationship between the four key soil functions and methods of soil sanitation. It depends on chemical properties of reagents used in this approach whether they make use of certain soil functions, influence or even jeopardize them. Parts of the changes thus imposed to soil are irreversible.

Kind of soil function	Method of sanitation	Principle of approach/reagent	Is the soil function employed for sanitation purposes?	Soil function gets altered in a positive or negative sense
Ion exchange	Soil washing	Tensides	Yes, insofar as ionic tensides are used to remove ionic pollutants	Anion exchanger positions get occupied by ionic tensides which are hard to degrade by bacteria
		Supercritical solvents	Elution is enhanced during and by formation of HCO_3^-	No; salts are hardly dissolved
		Alkali metals or calcium dispersed in liquid ammonia	NH_4^+ forms, cations are exchanged	None which last for long as ammonium ions undergo biological reoxidation
	Soil incineration	Thermal treatment to oxidize (combust) organics and turn sand, clays into ceramic materials	No	Organic ion exchanger sites are destroyed completely, most inorganic ones (clay) likewise
	Microwave heating	Heating is directed by absorption features to moist sites and those containing certain salts, solid (p-type) oxides	Ions are thermally mobilized	No effect except heating is so long and pronounced that decarboxylation of carboxylic acids takes place
	Phytoremediation, bacterial leaching	Extraction and immobilization of pollutants using growing biomass	Ion exchanger properties are crucial for growth and nutrient supply to growing plants and thus their capacity also to absorb substantial pollutants	No lasting effects, possibly reservoirs are replenished by fertilizer applications

pH buffer	Soil washing	Tensides	Rather an obstacle in applying ionic tensides	No effects by non-ionic tensides
		Supercritical solvents	No	No interaction, possibly some HCO_3^- does form
		Alkali metals dispersed in liquid ammonia	Reduces side reactions which would occur in staunchly acidic soils	Effects are relieved
	Soil incineration	Thermal treatment to oxidize (combust) organics and turn sand, clays into ceramic materials	No	Inactivation and outright destruction of both organic and inorganic buffer system (vitrified silicates or phosphates do but hardly buffer proton flows still)
		Spatially directed heating	Shifts buffer equilibria	Effect is almost fully reversible
		Extraction and immobilization of pollutants using growing biomass	Buffer activity is an obstacle to bacterial leaching	No effect concerning phyto remediation but acidification in bacterial leaching
	Microwave heating			
	Phyto remediation, bacterial leaching			

(Continued)

Table 2.8 (Continued)

Kind of soil function	Method of sanitation	Principle of approach/reagent	Is the soil function employed for sanitation purposes?	Soil function gets altered in a positive or negative sense
Reductants (encountered in lower soil levels)	Soil washing	Tensides		Low-molecular organic reductants are partially leached while Mn^{2+} or sulfides remain on site
		Supercritical solvents	No	See above: selective extractions of some organic reductants and sulfide mobilization
		Alkali metals dispersed in liquid ammonia	(Fast and powerful reductant itself)	Solvated electrons reduce soil components like Fe(III) and thus increase reductive capacity for long
	Soil incineration	Thermal treatment to oxidize (combust) organics and turn sand, clays into ceramic materials	Yes, organics get incinerated as substrates	No longer present after incineration
	Microwave heating	Spatially directed heating	Yes, contributes to ongoing reactions	Gets reduced
	Phytoremediation, bacterial leaching	Extraction and immobilization of pollutants using growing biomass	Phytoremediation takes place in upper (usually oxidizing) soil levels except for sewage irrigation sites	No effect

Reservoir for water and mineral nutrients	Soil washing	Tensides	No because tenside solutions introduce additional water	Increased water content, extraction of certain salts (nitrates, chlorides) is likely
		Supercritical solvents	No discernible effect	No extraction of salts
		Alkali metals dispersed in liquid ammonia	Larger amounts of water inhibit reaction; mineral nutrients and pollutants are partially reduced to element	Decreased water content, ammonium ions are enhanced
	Soil combustion	Thermal treatment to oxidize (combust) organics and turn sand, clays into ceramic materials	Clays and sand are important for occlusion and permanent immobilization of heavy metals	Barren, dry, mineral nutrients mostly inaccessible after treatment
	Microwave heating	Spatially directed heating	Water absorbs radiation selectively and thus is involved in directing heating and evaporation effects	No change imposed
Phytoremediation, bacterial leaching		Extraction and immobilization of pollutants using growing biomass	Minerals are leached while possibly binding organics in the same turn	Minerals are leached



Figure 2.14 A mobile soil washing plant assembled on a lorry. Overall length is some 14 m, and it weighs in at 50 t.

- The soil is not depleted concerning nutrients because nothing but hydrocarbons and traces of some metal ions is leached;
- CO_2 , which moreover itself is a natural component of soil air, escapes from the sample almost completely, when the pressure is relieved;
- During pressure reduction elution agent and dissolved pollutants separate without any other measures to be taken.

A conventional (mobile) soil washing device, using water and tensides, is shown in Figure 2.14. Mobility is the key difference with respect to high-pressure vessels using supercritical carbon dioxide, allowing to bring the sanitation device to the site of pollution and damage rather than removing the soil and bring it to the cleaning device. Hence there is no need to relocate large amounts of soil at once.

2.3

A Comparison among Environmental Compartments: Phase Composition, Miscibility toward Key Reactants and Contaminants, Transparency and Biological Activity

Subsequently we shall compare the key chemical and physical properties of all the three environmental compartments air, water and soil (and biomass):

- *Air: evaporation, fast transport, condensation, rain washout, large photochemical turnover rates.* Air is rather homogeneous in chemical terms although there are pronounced horizontal and vertical thermal gradients. Since air is thermally

rather stable, oxidizable admixtures may be degraded by applying high temperatures, either with or without catalysts.

- *Water: dissolution* (also of various salts), *precipitation*, *slower transport*, *surface photochemistry* (activated by formation of complexes), *hydrolysis*, *adsorption to particles*; both distinctive chemical and thermal gradients exist already near to the surface. After thermal treatment, water is biologically inactive, yet becomes rather reactive toward organics if heated further under appropriate pressures ($T > 250^{\circ}\text{C}$ and supercritical-fluid state), especially if O_2 is added to the mixture.
- *Soil: hydrolysis*, *adsorption to particles*, *precipitation* and separation of hardly soluble phases, *immobile*, no photochemistry except for the very uppermost millimeters. Soil is thermally almost homogeneous except for a thin surface layer of 1–2 mm, whereas there are pronounced chemical gradients; soil is sensitive toward thermal treatment, leaving behind usually irreversible changes of soil texture and of clay minerals. Unlike the fluid environmental compartments, lasting chemical effects can be caused in soil by simple mechanical treatment: compression of air brings about oxygen depletion also in topsoil, formation of sulfide and much reduced water permeation rates and coefficients. As a result, chemical gradients get much steeper than before.

Biomass cannot be taken as an environmental compartment but takes part in matter flows in a way which strongly influences stability, resilience and burdens of the “actual” environmental compartments, most so concerning soil. As for environmental engineering, this has practical implications (phytoremediation, environmental biotechnology, etc.). Hence biomass is reviewed here in context, analogy and parenthesis with the environmental compartments.

These latter environmental compartments pass quite different xenobiotic substances into biomasses also; metabolism there adds biotic modification and degradation processes to those which are abiotic in origins. Notably, biomass produces large amounts of substances which themselves strongly interact with xenobiotics, be it by simple cumulative dissolution (haloorganics in lipids). Furthermore, such interactions can include all resorption, active metabolism (like conversion into hydrophilic derivatives by linking sulfate ion, glycine, sugars etc. to non-polar, particularly to aromatic compounds) and finally remains or metabolic products of organisms cause adsorption (heavy metal ions on chitin) or precipitation (Mg, Ca, Cu with fatty acids, oxalate). The latter transformations obviously are directly related to soil as an environmental compartment.

The environmental compartments can be compared likewise considering their respective internal structures. Such structures can be formed by virtue of:

- Membranes within biological materials;
- Stratification of soil;
- Thermoclines and possibly chemoclines (haloclines) in water.

If there are such structures, both the transport rates and the chemical conditions that some potential pollutant is exposed to start to depend on the site where it is

at the moment. Of course, it is impossible to make completely general statements for any of the three environmental compartments which would apply everywhere between both poles, from littoral to deep-sea grounds and so on. Nevertheless it is feasible to identify such structures—associated with chemical and other gradients—in certain smaller regions and to use these structures in environmental technology or even create them purposely.

Table 2.9 gives a comparative list of the physical and chemical properties and biological activity in the three environmental compartments and in biomass.

Now let us have a closer look on this, comparing the environmental compartments in their above listing. Pronounced turbulence and fast circulation of air act against formation of chemical gradients. Matters are different with thermal gradients as these are due to adiabatic compression or expansion just by onset of vertical circulation⁵⁶). Although temperature differences will also shift chemical equilibria, both T differences and absolute temperatures are too small to cause corresponding effects here, with them additionally obscured by that very large deviation of Earth's atmospheric composition from the local thermodynamic equilibrium (LTE) by photosynthesis and biological release of CH_4 , H_2 . Matters are different on Venus and the three strongly convective gas planets Jupiter, Saturn, and Neptune (the atmosphere of Uranus is stably stratified rather than convective): CO (by $\text{CH}_4 + \text{H}_2\text{O}$ carbonization), PH_3 , AsH_3 , and GeH_4 (by high P , high T hydrogenation of phosphate-, arsenate- or germanate-containing dusts in the atmosphere) form at deep layers ($T \geq 1000 \text{ K}$) and are transported by convection back to the troposphere of the gas giants where they can be observed by spectroscopic means. In "our" air chemical gradients can only form and in turn influence lifetimes of atmospheric pollutants and other trace gases if either photochemical processes occur within a very limited vertical area or reservoirs of reactive substances get into the atmosphere. The principal sites—except for emission sources of anthropogenic pollution—for this are volcanoes and, especially, sea spray exposed to UV radiation which gives rise to lots of OH radicals and to quite peculiar atmospheric trace gases including BrCl (bromine chloride) and halogene nitrates ClONO_2 and BrONO_2 , all being highly reactive, and to stable compounds such as carbonyl sulfide COS . If turnovers sufficient to cause formation of chemical gradients in an agitated medium are to occur, conditions must change steeply in a small area or there must be strong UV absorption by likewise thin layers of matter. In addition, there should be direct contact to another medium (actually, another environmental compartment) which bears large concentrations of volatile compounds or those which can be dispersed as an aerosol.

What, then, is the role of any internal structure [from "simple" air–water or water–sediment interfaces over photoactive (thylacoid) biological membranes up

56) Convection bringing about vertical circulation starts exactly when vertical heat flow exceeds the limit of thermal conductivity at the given $\Delta T/\text{altitude}$ gradient. Absorption and release of thermal energy are increased in

atmospheres of Earth and Titan by evaporation (surface) and condensation (cloud formation somewhere above) of water and methane, respectively, transporting much of the latent heat.

Table 2.9 Chemical, thermal and biological spatial differentiation and pattern formation in the three environmental compartments and in biomass [extent and ramifications; from Fränze, Markert, and Wüschmann (2005)].

Compartment	Formation of chemical gradient	Formation of thermal gradient	Mobility of main component	Biological activity in environmental compartment	Results of heating
Air	Only in very dry air or just above isolated ocean surfaces	Adiabatic: 7–9 K/km (negative)	Large (typically of order 5 m/s)	Almost none	Thermally stable except for some trace gas components
Water	Formed by photosynthesis (surficial supersaturation by O ₂) and by thermo- or haloclines	Thermal gradients only next to surface; deeper layers defined by density maximum of water	Different (some cm/s up to m/s) (rivers, tidal flows, ocean currents like Gulf or Kuroshio streams)	Large and multiple	Oxygen depletion, loss of biological activity; activation of degradation processes at several hundred °C
Soil	Yes, particularly when going into permanently wet layers	Only close to surface, deeper below soil temperature = surface air annual average temperature	None	Very high, controls pedogenesis and further evolution of soil	Soil biota is damaged and destroyed; dehydration and sintering of clay minerals
Biomass	Gradients exist on all hierarchical levels (organelles, cells, organs) – pH gradients in the intestine to blood vessels around! – and also toward environment	Specific organs in homoiothermic animals (liver is hotter in mammals)	Sometimes very pronounced (in animals) while it does not exist in others or occurs almost passively (aquatic drift of plankton, bacteria)	Large by definition	Usually most sensitive

to films of photoexcitable compounds like PAHs spreading on a water surface] in producing chemical processes, chemical gradients and finally achieving purification of this environmental compartment? If there is photochemistry with large photo-absorption shares in a thin layer, a chemical gradient is likely to form even against turbulent mixing. This likewise holds for aquatic photosynthesis and for photochemical reactions in an atmosphere which cause smog formation (Los Angeles smog), owing to the simple fact that the remaining amount of photoactive radiation intensity available on the next volume below to be passed by light is not decreased linearly but follows an exponential pattern (Lambert–Beer’s law).

Smog does stabilize itself owing to its strong light and UV absorptions. As noted above, seaspray provides a reservoir of reactive compounds to get dispersed in the lower atmosphere, including halogenes and BrCl (Sander *et al.*, 1999). Thus there are steep gradients of concentration levels also of highly reactive oxidants. Some well known photooxidants such as peroxyacetyl nitrate ($\text{CH}_3\text{--CO--O--O--NO}_2$, being the mixed anhydride of peroxyacetic and of nitric acid) hence also occur over ocean surfaces in clean air, most remote of any atmospheric pollution sources.

Chemical and thermal gradients control kinetics and sites of certain chemical reactions in the environmental compartments. Biological activity can be increased or suppressed thermally while light creates chemical gradients in water and air by being used in photosynthesis and abiotic photochemical processes. Pollutants which get into the environmental compartments then to migrate through them vertically will pass these gradient regions sooner or later, get degraded or become trapped in biomass, soil and water if there are solubility differences among partial volumina. Hence it is a key approach in environmental engineering to construct or enhance such gradients next to a pollution site.

Table 2.9 shows that water and soil differ from air by their much larger extents of biological activities; atmosphere thus is not an ecosystem. Biological activity in soil will be involved in creating chemical gradients if organic matter is present to act as a reductant. In soil (except for pure sand) this always applies owing to the content of organic matter, while in water a second necessary condition is to interrupt total circulation and thus oxygen supply of deeper layers. If the biota would not take part, most oxidative reactions of organic compounds common in the environment with either oxygen or nitrate would be too slow—if not photoactivated—that relatively faster diffusions of both oxidants and reaction products would preclude formation of a reaction front⁵⁷⁾ and thus of a chemocline.

Things get different as soon as living beings are involved, just due to physico-chemical implications of reproduction (cf. Fränzle, 2010). Besides largely enhancing the rates of corresponding processes, reproduction will increase turnovers with

57) Reaction fronts are related to autocatalytic reactions, whether autocatalysis be induced by simple autocatalyst species like protons (H_3O^+) or by reproduction of organisms which make use of the given reaction. For example, commonly around the chemocline of a common lake in summer or winter there are few organisms,

allowing H_2S and NO_3^- to co-exist over depth bands in water which are several meters thick but in the Black Sea intense bacterial activity at the interface (chemocline) reduces this mixing region among strong oxidants and reductants to $\ll 1\text{ m}$ (Murray *et al.*, 1989).

time as long as there is net growth of biomass. This is called an autocatalytic process which can give rise to formations of chemical wavefronts⁵⁸⁾ which produce sharp gradients at their (present) edges anywhere in those environmental compartments which are dominated and, thus, shaped by biological activity. Hence sulfate reduction will not just become confined to some parts of the volume which is available, but kinetics also become most non-linear. Hence it is very hard to predict to which soil horizon a chemical poured/spilled somewhere on the ground will get at most, let alone, how fast it is going to be degraded at this terminal point (assuming vertical migration is not stopped by impermeable barriers like clay or loam, of course). Often degradation has to be studied by means of modeling experiments; as a rule, cultivating and feeding (for co-metabolism) local consortia of microorganisms which are already present at the site is more effective (EPA, 1997) than selecting pure cultures meant to achieve best turnover of pollutants in conditions which use to differ from those at the given site. Such an approach to make use of local conditions, corresponding microorganisms which already had undergone adaptation and selection at the site to degrade xenobiotics *in situ* is called "natural attenuation".

Conclusions

Gradients are most important in environmental engineering since every process which is going to remove a substance already emitted to the environment again from some compartment will also create a concentration gradient. Often one succeeds to create it only if the inflow of competing reagents (e.g., sulfate to be used as a biological oxidant rather than the far more effective dioxygen) is blocked by some barrier. This actually is done during de-acidification of lakes or, rather, ponds which were charged with sulfuric acid geogenically after their being created from open-pit mining, like in Lake Barleb (Saxony-Anhalt, Germany). Acidic waters are pumped off from under the thermocline (natural gradient), contacted with organic substance (straw, etc.) with sulfate reducers present, then to cover the sulfidic sludge against re-oxidation by air, before refilling the water and remove remaining HSO_4^- by liming. Methods like reverse osmosis (in both water cleaning and sea-water desalination) which produce new concentration gradients cannot be done unless employing membranes and adding mechanical energy (hydrostatic pressure). More generally, gradients can be introduced into matter mixtures to purify them by introducing membranes into the matter flows and pass energy through them to increase the extent of separation. Otherwise, controlling admission of certain possible reactants to some sites will also cause gradients to form, that is, between those sites where a certain reagent is available, and others where

58) Such chemical reaction fronts which exhibit chemical properties rapidly changing with site while slowly propagating can appear in quite different sites in living nature, from the edge of

mould cultures growing on agar or bread up to starting of biogenic horizon formation and stratification in soils just recently deposited.

it does not get to, and hence other modes of reaction are taken instead, for example, among different parts of a sewage treatment plant which vastly differ in redox potential due to O_2 getting there (nitrification) or not (denitrification, fouling tower).

As mentioned before, things are hard to predict, especially concerning the range of pollution until natural barriers or sites/conditions suitable for degradation take over, with transport rates in soil being very slow. Hence it must be emphasized that the key issue of soil protection is not to conceive ingenious methods how to clean up soil but to avoid emissions into soil as much as possible (including accident precautions) and to identify old polluted sites, because they cannot be readily seen, smelt or detected by the surface analyses used with air or water. Given the lack of photochemistry (except, perhaps, in wells) and poor transport kinetics, a secondary purification of compact soil and of ground, trickling or well waters is far more difficult than in the more open and accessible fluid systems. Nevertheless, there are some methods specifically designed for soil clean-up, namely:

- Rusty walls (reactive barriers; cf. Section 4.3.1), usually made of iron filings/gravel mixtures which retain heavy metals, certain non-metals including As and halogenated hydrocarbons by chemical reactions with Fe oxidation, precipitating the insoluble pure element or oxide or producing less halogenated, less toxic secondaries;
- Extraction by means of plant roots which, obviously, is restricted to those layers of soil or groundwater roots get access to, with the plants harvested and removed later on, along with the absorbed pollutants (phytoremediation).

3

Innovative Technologies

3.1

Criteria for Innovation

In terms used by economists, the distinction between innovation and invention is given by the condition that the former (innovation) is about and requires putting something new onto the current market, be it a procedure, a device, part of a device or a novel material to fulfill some task. Say, a new kind of semiconductor for photovoltaics or light emission devices or a biogenic substitute for ores or petrogenic polymers. Unlike with some inventions, one actually has to sell and (hopefully) make money with it, rather than just conceiving something new (at least new at a national level) and construct some prototype (which is tantamount and sufficient to having some invention). Hence, innovation requires invention but only some (small) share of the inventions will actually make it to the market, let alone succeed in competition among the technologies on the market. In environmental technology, invention may sometimes be promoted, demanded and also—concerning the items and problems—guided and even shaped by new legal requirements. These legal requirements in addition will facilitate the “conversion” of inventions into innovations because classical market competition criteria are partially levered. Accordingly, the item or procedure or device must both be new and able to compete against solutions which are already more or less established. However, there are (hardly?) any ideal markets, nor are there completely informed, rationally deciding stake-holders or consumers, as assumed by classical economists; the deciders are more difficult and less rational, less accessible to being convinced by technical arguments, than perhaps they should be.

Environmental technology, and corresponding inventions and innovations thus get into a particular dilemma: up to some extent (and from the viewpoint of some parts of the population, electorate and also political parties who disagree on this political approach on demand) the ability to compete can be substituted by mere political intention. But this exactly produces new problems of legitimation even though one (apparently) has “green” ethics and criteria of sustainability (Rio Declaration, 1992; see below) backing introduction, for example, when funding electricity from photovoltaics although it is some five to ten times more expensive than from fossil sources yet. If this technology (or some other) perhaps does not

really pay to avoid larger parts of pollution (how large now is relative CO₂ substitution by solar water heating in Germany or even Scandinavia?) or if it goes into removing the last traces of pollutant legitimization [people in Germany are proud now to have limited the 2,3,7,8-tetrachlorodibenzo(p)dioxin (TCDD) venting from the *total* of domestic municipal waste incinerators to less than 10g/year!], and ethical issues of directing limited monetary resources to such technologies arise again: up to what limit of funding can be justified in order to introduce, scale-up or apply some technology? Further, environmental economics also deals with the monetary equivalents of “services” produced by living nature which they (presumably) provide most efficiently if left alone (Costanza *et al.*, 1997; Vester, 1986). The estimated total of these services being priced about as high as the combined human economic activities (some 30 trillion €/year), which 1:1 ratio, by the way, compares to the fact that roughly half of photosynthetic primary productivity is used by man for food, feeding husbandry, or in the food chain of fishes which then are caught. Inventions meant to address environmental demands from scratch are rare at best.

As noticed before, it is innovation which really can alter societal and environmental statuses, so the task actually is about enhancing the chances of inventions to become environment-related innovations rather than (although this also is important) trying to increase the numbers and rates of inventions related to environmental chemistry and technology, respectively. This latter approach also guides the funding policies (and, corresponding guidelines) of institutions like the Deutsche Bundesstiftung Umwelt [the German Environment (Research) Foundation, endowed with a capital stock of some €1.5 bio. coming from formerly state-owned enterprises going public]: make things practical, on whatever level or scale, not so much invent something “really” novel.

In the long-wave (Kondratiev) pattern of global economy driven or influenced by innovation (Kondratiev, 1926; Berry, 1991) this corresponds to periodic changes of the selection conditions for inventions (which presumably occur all the time at approximately constant rates) to become innovations, even fundamental ones, capable of propelling an upsurge of global economy which is then to last for a couple of decades. While it remains to be seen whether environment- and/or health-related (Nefiodow, 1991) innovations can trigger yet another “long wave” by themselves, it is obvious that both political prerogatives and the demands of a growing world population—especially in the largest developing countries now partly having passed the threshold into industrialization, like China, India, Brazil, countries which are partly doing so (especially in military and transport terms) on the most advanced levels and partly paving new ways rather than repeating patterns of industrialization which were done elsewhere—require the translation of invention into innovation in a more efficient way.

3.1.1

Sustainability

Sustainability is a term or criterion which was originally (eighteenth century) introduced in topics of forestry: remove/cut only as many trees as can reasonably

be expected to re-grow in the same period of time on the site, thus maintaining a kind of equilibrium state. This criterion or state of affairs obviously cannot be applied one by one to any kind of economical activity which makes use of non-renewable resources, be it (e.g.) production of energy by fossil fuels or ore processing. Here the end of a (more) sustainable economy takes either replacement by sustainable sources of matter and energy (Section 4.4) or a considerable extent of recycling.

Acknowledging that “ideal” sustainability is not at hand, the alternative then is to compare among different old and new options to do or organize something which are likely to include partial use of regenerative resources and estimates of the irreversible effects one item or one good of service will produce from being produced up to removing the remains left after (cradle to grave analysis). As a rule, it is very difficult to do this in a both comprehensive and generally convincing way, at least if effects far extend the time-scales of political decisions and planning: foreseeing several 10^5 years, even lignite becomes a regenerative energy source, as the lakes left after open pit mining are then going to fill up with sediments and peat later on spontaneously turning into lignite once again. Or, over which periods of time precautions can or should be calculated concerning expenditures and workforce to safeguard deposits of radioactive waste? Obviously both the estimated “actual” price of nuclear fission energy/kWh and the aspect of realistic safeguarding critically depend on this.

More easy to handle than a full-scale cradle to grave analysis with respect to given technologies, raw materials used to realize them and actual sources of these raw materials, including fossil sources of energy, is the idea and concept of “ecological footprint” (Schmidt-Bleek, 1992): how much material is relocated, excavated, removed, separated, processed and, for the largest part, eventually (actually, all too soon) deposited in producing 1 kg of a certain item? For example, how much ore and “numb” stones are moved to get 1 kg of gold, or some platinum group metals, how much water, fertilizer and fossil energy carriers are consumed in growing 1 kg of orange fruits at given semi-arid site x and so on? The factor known as ecological footprint can be very large ($\gg 10^5$). Often costs and side-effects of transport substitute for unwanted effects of doing something in a “conventional” way: from aspects of fossil fuel consumption and CO_2 release, it does not matter whether oil is consumed to make fertilizers (or, actually, release the H_2 required to produce ammonia) in classical agriculture in Central Europe or else to transport “greenly grown” apples from New Zealand or Argentina to our hypermarkets, including cooling, covering with protective gases and packaging for long-distance travel—provided amounts are similar.

Even when only comparing the spatial density of energy flows in densely inhabited industrial societies to the flux of sunlight available in, for example, Belgium or South Korea, one soon sees that sustainably running an economy in the manner we are accustomed to live is outright impossible. Things get even worse by pseudo-solutions apparently meant rather to protect and benefit classical ways of economy than actually to achieve a better degree of sustainability: everybody should be aware that the chemical energy efficiency of photosynthesis, if run in an extensive mode (without massive application of fertilizers) is less than 1%. This, and the

corresponding requirement of areas, does not too well compare to the efficiency of a system using polycrystalline photovoltaics to generate electricity for water electrolysis and then combine H_2 to CO_2 to obtain methanol or other kinds of fuel, or even electroreducing CO_2 directly into CH_4 or CH_3OH by photovoltaics: this will earn 7% and more of incident solar light. Thus, about one-tenth of the area on which now rape or corn are grown for purposes of fuel production will do. Is the production of “eco-gasoline” or “bioethanol” about subsidizing peasants or, really, about providing more eco-friendly fuel sources, then?

3.1.2

National and International Jurisdiction

As mentioned before, jurisdiction and law-making are principal incentives for turning invention into innovation in the realms of environmental technology, often actually replacing economic advantages. Given this, it must be investigated how these extra-market incentives work and what will happen if:

- 1) There are agreements for environmental measures on very large, say European Union (EU), or even global scales;
- 2) There is a conflict of demands thus procured with limited resources (e.g., the three-way catalytic exhaust gas converter cannot even be attached to all the cars now around in the world on four-stroke Otto engines simply for lack of all the platinum group metals involved, Pt, Pd, Rh).

Of course, when there are problems which are likely to bother all mankind, regardless where they live, or reasons thereof are spread all over the world, it is hard to argue in favor of national and against global legislation, agreements. As seen in climate-change issues, such agreements are very hard to obtain but things cannot be tackled on smaller scales efficiently, not without compromising both the acceptance of international right and law-making and the efficiency of the agreements, regardless what the latter mean for living conditions in the developed world.

Both legislation and jurisdiction are still developing even the most urgent and fundamental kinds of answers for environmental demands on various scales, especially so far as international law is concerned. Doing harm to the environment or modifying it altogether is no longer taken to be a “domestic, internal affair” of some state when its effects extend beyond the borders. It already was doubtful whether what happened to Lake Aral (Figure 3.1) by extracting too much irrigation waters from rivers Amu Darya and Syr Darya. Causing regional desertification and eolian transport of salts over large distances, could be taken as an internal matter of the late USSR, but it surely is not an internal affair of Uzbekistan now, with the damages (salt impacts, climate changes) caused thereby extending beyond both Uzbek and former Soviet southern borders.

In earlier times, international legislation and the law of peoples often had to deal with states going to vanish by occupation (could they actually do so under some regime of international law, considering, e.g., pre-WW2 Czechoslovakia, or

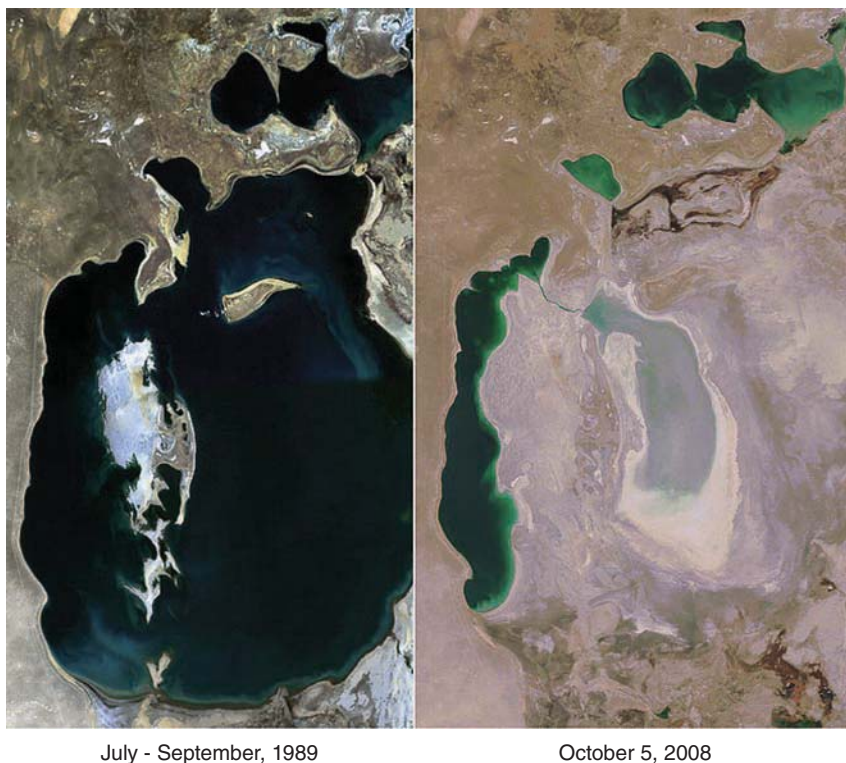


Figure 3.1 Comparison of the Aral Sea between 1989 and 2008 in Kazakstan/Uzbekistan (photos taken by NASA). In former times the Aral Sea was one of the four largest lakes in the world. The sea has been

steadily shrinking since the 1960s after the rivers that fed it (Amu Darya and Syr Darya) were diverted by Soviet Union irrigation projects.

Tibet, or more recently Kuwait?). But what about the now imminent risk that independent (clusters of) islands (Tuvalu, Maldives) or low-lying coastal states (Bangladesh) be inundated altogether? Would, in terms of international law, this make them disappear as subjects of international right as the latter requires:

- 1) A government in actual charge of the territory;
- 2) An indigenous or long-settled population (an uninhabited Arctic or Antarctic island thus cannot be proclaimed to be an independent state);
- 3) Controlling a territory of mainly natural origins (disallowing proclamation of states on artificial islands or similar constructions which had been attempted several times indeed).

If condition (3) is removed by rising sea levels [and likewise condition (1)], which has already prompted the Maldivian government to have a ministers' meeting

right down on seafloor), do then states like the above simply cease to exist, and who then is to blame or construct alternatives for the inhabitants who obviously must leave to somewhere else, and who is to pay this?

Cross-border environmental damages cause issues of liability likewise, and domestic or EU-level legislation and jurisdiction also deal with liability issues. When regaining their independence from the USSR (in 1988–1991), Estonians actually used the following way of argument: environmental damages due to oil shale and phosphorite minings were such that ethnic Estonians—as stakeholders—could no longer even theoretically agree with other (more or less, external, i.e., Soviet) authorities passing legislation, administrative decisions and subsequent mining activities on their [Estonian (-SSR)] territory as the further existence of this people [condition (2)] was possibly at stake. This argument then was soon extended to the level that USSR legislation was void there altogether (16th November 1988) unless accepted by the Estonian Supreme Soviet in very specific, single cases (Helme, 1991). Indigenous people living in primary forest regions all over the (tropical and boreal) World nowadays argue quite similarly, for example, in Brazil or India or Siberia, even if not considering to found or re-found independent states.

3.1.3

Cost/Benefit Calculations

Apart from lacking availability of particular materials required to do something, many things can be done in quite different ways. However, it is an issue which relative as well as “absolute” reduction effect with respect to environmental burdens can be effected using one more Euro (€) in this or that manner—or site. During the transformation of formerly socialist economies in Eastern Central Europe and the Balkans, the then European Economic Community (EEC)—both anticipating these countries to join the EU some later day (which would come in 2004+) and trying to protect its own territorial waters (e.g., Baltic Sea) against pollution—made up large programs concerning technical protection of environments. These schedules include(d) coal, lignite power-plants equipped with filters, desulfurization gear and constructing lots of sewage treatment plants not only next to EU border rivers, (correctly) estimating that even the (EU-internal) benefit ($-x$ g SO_2 or $-\gamma$ g phosphate per €) would be much higher than could be gained in trying to bring the corresponding plants within the then EU to the utmost levels of technology which could be bought.

The same problem is observed in many highly developed countries: is it still actually worthwhile to “optimize” (with respect to mere efficiency rather than cost–benefit ratios) environmental protection and clean-up measures, or should we rather support less developed neighbours to improve their situation, especially if we are interconnected with them by dominant wind current directions or along rivers flowing across borders? One might argue that the latter, for example, rivers like the Bug or Odra, is mainly a European kind of problem given that, for example, Japan, New Zealand or Australia are surrounded by oceans while the big

United States or Canadian rivers will not come in from less developed ones polluting them although the Rio Grande forms the United States/Mexican border over long distances but normally the situation is the other way round: the Colorado River does not generally make it to Mexico, let alone to the Pacific Ocean. The same with the Middle East: although Turkey is responsible for quite a deal of pollution in the rivers Tigris and Euphrates, the latter then flow into less developed countries (Syria, Iraq, Kuwait).

As carcinogenic compounds or phenomena (i.e., ionizing radiation) do not have either a linear dose–effect (likelihood of actually contracting cancer) relationship nor a threshold dose/concentration below which their presence would be entirely safe (yet, like benzene, might occur in the unpolluted environment, also), this way of reasoning by dividing removed or avoided pollutant per currency unit which is invested for this purpose, however, cannot be applied simply, linearly, to whatever environmental problem—and many of these are related to carcinogenesis. Here, one has to strive for risk minimization, that is, achieving the lowest technically possible (be it front of pipe or end of pipe) level of pollution related to some area of human economic activities becomes mandatory. Of course, this cannot be done at any cost practically. We are left with compromises going to be negotiated, sometimes, of course also negotiated in court. This in turn requires a sound, detailed pertinent legislation underpinned by corresponding political will.

3.2

Examples of Innovative Environmental Technologies

Understanding chances, limitations and reaction mechanisms pertinent to environmental engineering, in particular chemistry, requires to know and understand quite a number of basic chemical concepts. Rather than focusing on seemingly elementary, anyway fundamental, but hard to grasp phenomena such as covalent chemical bonding emphasis will be laid on quantifying description of similarly fundamental phenomena and their applications in environmental engineering. From there we can embark to discuss dimensions and designs of typical, common or benchmark-setting devices or plants in environmental engineering. Reaction mechanisms will only be considered insofar as limiting conditions for running or catalyzing some process are related to them, such as in general acid catalysis. Whereas most of these basic concepts apply to both organic and inorganic compounds, some are restricted to certain classes of compounds which are important to deal with in environmental chemistry and sanitation for reasons of toxicity, mutagenic activity, sheer mass or secondary adverse effects, like aromatic hydrocarbons. While reaction kinetics of the latter can readily be described to depend on substituents by the Hammett equation, there are no similarly simple or reliable approaches for other kinds of substrate compounds. Due to the importance of these compound groups corresponding description approaches merit their mentioning and place in books like this as some extent of quantification is required even to estimate whether certain approaches of environmental sanitation

are feasible at all, or which reagents bring about more toxic or more refractory secondaries.

We hence begin to investigate key features of immobilization, namely precipitation, adsorption and other methods. Then we are to distinguish between dimensions of static (i.e., thermodynamic) and dynamic (kinetic) stabilities of certain kinds of matter, as depending on redox potential controlling the possibility of certain electron transfer reactions. Kinetic stability of benzenoid aromatics toward environmental agents like OH radicals as well as biochemical oxidations by, for example, laccases is discussed directly afterwards. Beginning with just formal kinetics (the Hammett equation) we thereafter consider the phenomena which influence reaction/transformation kinetics in a natural environmental setting. These phenomena, familiar from physical chemistry, include both the derivation of an activation barrier against chemical reaction and the chance to reduce this barrier (at least for one or few of the possible reaction pathways) by selecting and introducing an appropriate catalyst. Increasing product selectivity by selective catalysis has many features in environmental chemistry:

- 1) Selective syntheses bring about less coupling products which may be simply a nuisance as they have to be removed or sold separately.
- 2) Among, for example, the possible products of NO_x treatment end of pipe of internal combustion engines or fossil fuel power plants, using hydrocarbons or H_2 as reductants, it depends on proper choice of catalyst whether harmless N_2 , the long-lived (≈ 200 years in the troposphere) greenhouse gas N_2O or highly toxic byproducts HCN, nitriles would form.

Cleavage of contaminants from the environment means to remove certain chemical species from a reaction mixture on either a steady or periodic schedule. But then chemical equilibrium will (can) no longer be attained but we are concerned with throughflow equilibria and corresponding problems in running a process in a controlled manner, when oscillations, pulsating kinetics, other nonlinearities and even chaos become possible. In order to link this to environmental engineering, each of these sections on chemistry will close with some conclusion which outlines features and ramifications of this in technical environmental chemistry, including difficulties and by-products which might arise by applying that particular strategy. Thus, the forthcoming chapters on case studies focusing on applications of these principles for protection of environment get prepared to the reader.

The case studies deal with certain compounds, technologies and environmental problems caused or addressed by them. Of course, these are just examples selected for a couple of reasons, including the authors' own fields of work. There are many more techniques and problem, in fact so many that it is impossible to give something like a comprehensive treatise on environmental engineering now—if one is actually focused on presenting all the techniques rather than the pertinent principles as we thus chose to do, the respective examples being mentioned just to show how “first principles” translate into practical solutions.

3.2.1

Precipitation, Adsorption and Immobilization

A main task in environmental engineering and technology is to keep potentially hazardous chemical substances (and radionuclides)—if their production cannot be avoided altogether—from spreading freely into environmental compartments or the biota. This requires to make them immobile in the environmental compartment where they happen to be or be produced now. Options to achieve this include:

- *Precipitation* into some hardly soluble phase;
- Binding to an interface by *adsorption*. This may also occur in pores of some porous sorbent (absorption), for example, in active carbon or zeolith silicates (water softening), or:
- Producing covalent bonds to some support which itself may be hardly soluble and/or polymeric (*immobilization*).

The latter solid polymer may be some natural organic material such as peat, lignite or a humic acid, but also a sulfide mineral. The various ways of binding depend partly on interface effects, partly on chemical reactions.

3.2.1.1 **Precipitation**

Precipitation does occur if two hydrated ions (wrapped into water molecules), for example, react Ba^{2+} and SO_4^{2-} , to form a neutral ionic crystal with a lattice energy (here: 2.469 kJ/mol; cf. Table 3.1) large enough to overcome the respective summed energies of hydration/solvation.

In this case, the solid (barium sulfate, baryte) will be more stable than an array of dissolved ions. As long as ionic radii are rather constant, hydration (solvation) energies will be about *proportional* to ion charge, while the rules of electrostatic attraction have it that mutual attraction of gegenions and thus lattice energies will rather increase by the *product* of both ion charges (Figure 3.2). Systems (salts) which are constructed of doubly, triply or even quadruply charged ions thus are

Table 3.1 Aqueous solubility products ($T = 25^\circ\text{C}$) versus lattice energies of isoelectronic ion crystals of type $\text{M}(\text{XO}_4)^{\text{a)}$, with $Z(\text{M}) + Z(\text{X}) = 72$, namely cesium perchlorate (CsClO_4), barium sulfate (BaSO_4), lanthanum phosphate ($\text{LaPO}_4 \cdot 2\text{H}_2\text{O}$; a dihydrate) and cerium (IV) orthosilicate (CeSiO_4 ; extremely insoluble, cerite mineral).

Compound	Log of solubility product (–)	Lattice energy (kJ/mol)
CsClO_4	2.4	636
BaSO_4	9.96	2469
$\text{LaPO}_4 \cdot 2\text{H}_2\text{O}$	22.3	Ca. 7300 (GaPO ₄ 7381)
CeSiO_4	Hardly soluble at all	

a) Z: Ordinal number of element; M: metal; X: non-metal center of the oxoanion.

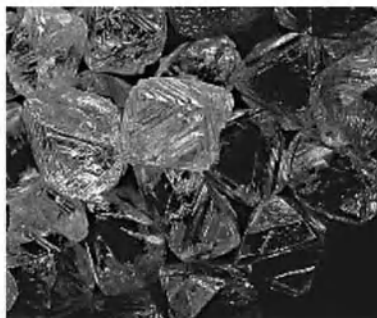
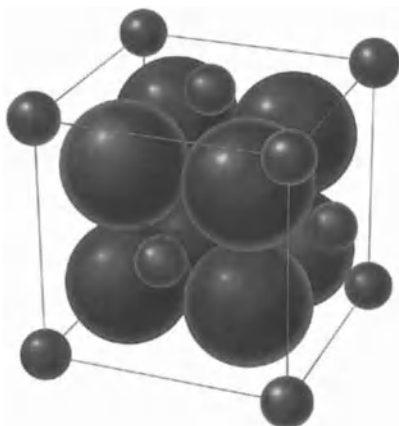


Figure 3.2 Crystal lattice. Left: schematic; right: diamond (covalent structure, same in solid semiconductors silicon and germanium). Ionic systems (“genuine” salts and

covalent macromolecules) tend to form similar crystal structures. Left photograph courtesy of: Hahn-Meitner-Institut, Berlin. Right photograph courtesy of: U. Freiesleben.

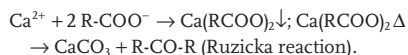
far less soluble in water (and will not dissolve in any other whatever polar solvent unless undergoing protonation or other chemical changes) if they are real ion crystals, unlike 1:1 aggregates of monovalent ions because lattice energy may no longer be compensated for by solvation.

Barium sulfate lattice energy is about four times, that of lanthanum phosphate even 11.5 times as large as that of cesium perchlorate. It can be calculated from differences of solubility products of LaPO_4 and CsClO_4 , that mixing of 1 M La^{3+} solutions (sulfate, chloride, nitrate) with 1 M PO_4^{3-} will release some 113 kJ/mol more of thermal energy than adding perchloric acid—which is completely dissociated in water—to a 1 M cesium salt solution. This is about half the formation energy of water from the elements!¹⁾ It is possible to convert this into a general strategy.

Precipitate the critical ionic environmental components by adding gegenions of the largest possible individual charge, with ideas on which gegenion should be applied being limited just by toxicity or price considerations. Phosphates are going to be precipitated during sewage water treatment by trivalent iron or aluminum

1) Excessive lattice energies can indeed tear off covalent bonds readily: azides (salts of hydrazoic acid HN_3) will explode to release N_2 , metal atoms already during crystallization or upon the slightest mechanical touch if the gegenion is too small while other, identical azidometallates with large gegenions withstand being hit by a hammer, and the small solubility of polycarboxylate salts of alkaline earths

(“lime soaps”), rare earth elements or (best-suited) thorium brings about carbonate cleavage upon heating, producing symmetrical ketones or cycloketones (from long-chain dicarboxylic acids) with a further lattice energy gain:



[rare earth elements such as La^{3+} would be both too expensive and highly toxic for aquatic plants, in particular algae (Cowgill, 1973), less so for zooplankton and fishes]. With their even higher +4 charge, soluble, for example, Na silicates, are an optimal “trap” for all kinds of more highly charged cations, di- and trivalent ones (with Al-forming clays) besides Ce^{4+} and thus are suited to immobilize fissionogenic radionuclides. Na silicates, “glass of water”, are then used as silicate source, with the silicates being stable toward radiolysis. Heating such salts of multiple-charge cat- and anions will make them melt, of course, but given the strong symmetric mutual interactions among the ions, it is unlikely that the original salt lattice structure will be recovered upon cooling. Rather, an amorphous structure will be produced, that is, a glass (cf. LaPO_4 glasses distinguished by their high optical diffraction index for optical instruments such as microscopes). This further enhances radiolytic stability: whereas a crystalline solid would become misordered (“metamictic”) during prolonged self-irradiation by ionizing radiation, a glass cannot suffer from such disordering as it is already disordered. Accordingly, such silicate or borate or phosphate glasses containing Sr, Y, rare earth element radioisotopes are expected to remain stable toward leaching of cations by ground water or even salt brines (storage of radioactive waste in salt diapirs possibly getting flooded!) for very long periods of time—until the radionuclides did decay altogether.

At sufficiently large individual charges anions also can induce precipitation of hardly soluble salts²⁾ also if they do not contain oxygen. Here, there is another mechanism besides rapidly increasing lattice energies which decreases solubilities in water and other polar solvents: mutual polarization of large, “soft” cat- and anions such as I^- , S^{2-} , Ag^+ , Pb^{2+} or Hg^{2+} which turns hard, colorless, brittle salts or minerals into rather soft, macromolecular, thus insoluble, colorful semiconductors (rather than electrical isolators which common salts are). In fact, these are covalent macromolecules rather than “genuine” ionic salts like NaCl, mostly inert toward attack by water or Brönsted acids (but readily reacting with alkylating agents like halogenated hydrocarbons). By semiconductor formation, monovalent anions like iodide or cyanide can form hardly soluble precipitates with certain soft, large monovalent cations (Cu^+ , Ag^+ , Tl^+), but more common are such semiconducting materials formed from similar divalent anions like sulfides of multiple-charge cations which precipitate once sulfate solutions start to undergo sulfate reduction. They accordingly also occur in a digestion tank, causing heavy metals to accumulate in sewage sludge. Finally, it should be mentioned that similar precipitations are also feasible using large (often, multiple-charge) organic anions such as oxalate, phenolate, polyphenolates including humic, gallic acids and so on. These are pertinent to environmental chemistry and water purification:

- 2) Another example from geology are arsenides and thioarsenides (As^{3-} salts like $\text{Cu}_{21}\text{As}_{10}$, As_2^{4-} species like loellingite FeAs_2 or AsS^{3-} containing ones like arsenopyrite) which readily form in hydrothermal veins

although AsH_3 is so powerful a reductant that it will not exist in any substantial concentration along common mineral-forming cations.

Phenols—including their oligomers of about 400–2000 molecular mass often dubbed anthropogenic humic matter when created, for example, in carbochemistry—readily precipitate with Fe(III). Hence adding iron salts to water bodies burdened by such organics will readily clean them, allowing to get light into deeper layers of these waters and start ecological revitalization. Almost all di- or trivalent metal ions undergo precipitation by oxalate, permitting to remove complex metal ion mixtures completely, with even traces captured by co-precipitation (later on, baking the oxalates will convert them into insoluble oxides). Oxalate precipitation also occurs in geochemistry: among the very few minerals with organic anions, two are oxalates [Ca oxalate = whewellite, Cu(II) oxalate = moolooite]. Here oxalic acid is the terminal product of controlled air oxidation of polymeric organic matters including lignite. Common intermediates are rather oxygenated lignites which release hardly any useful amount of heat upon combustion but may dissolve in appropriate organic solvents or even be almost liquid. The oxides obtained by baking undergo sintering and then once again are stable toward leaching of cations which is most significant once again in nuclear technologies (both Sr and Y, rare earth element fission products afford most insoluble oxalates, with part of the added oxalic acid used to reduce nitric acid burdens and chemical aggressivity of “nuclear broth” produced by spent fuel dissolution).

3.2.1.2 Adsorption

Mutual contacts between an interface of a sorbent—which is the material, commonly solid, binding the sorbate to its surface, for example, charcoal or active carbon—and the sorbate (all gaseous, liquid or also solid) also causes a polarization of the outermost electrons of both partners which contributes most to sorptive binding. As polarization will change charge distribution and binding energies inside the adsorbed sorbate molecules (physisorption), net charge can be transferred to or from the sorbent support to the adsorbed species, additionally influencing the construction of hydrogen bonds on sorbents like cellulose, clays or metal hydroxides and further increasing the attraction among sorbent and sorbate, up to about the energy of weakest covalent bonds which is about 50 kJ/mol.³⁾ From then on, kinks in sorbent surface will induce sufficiently strong binding to produce yet more charge transfer and actually break off given chemical bonds in the very first adsorption layers (Figure 3.3), inducing secondary chemical reactions beyond sorbent decay (chemisorptions).

If the mentioned effects on chemical bonds next to the interface become so pronounced to dissociate chemical bonds in the sorbate, parts of the sorbate molecule may turn into fragments which can remain next to the surface but move parallel to it slowly, allowing for an eventual recombination among the fragments thus formed (heterogeneous catalysis). However, physisorption often does suffice to effectively remove the sorbent from the environment irreversibly to clean it (application of clays or active carbon).

3) For example, chemical bond dissociation energy (BDE) about 0.5 eV in all Kr-F in KrF₂, N-N in N₂O₃, C-H in the formyl radical HCO.

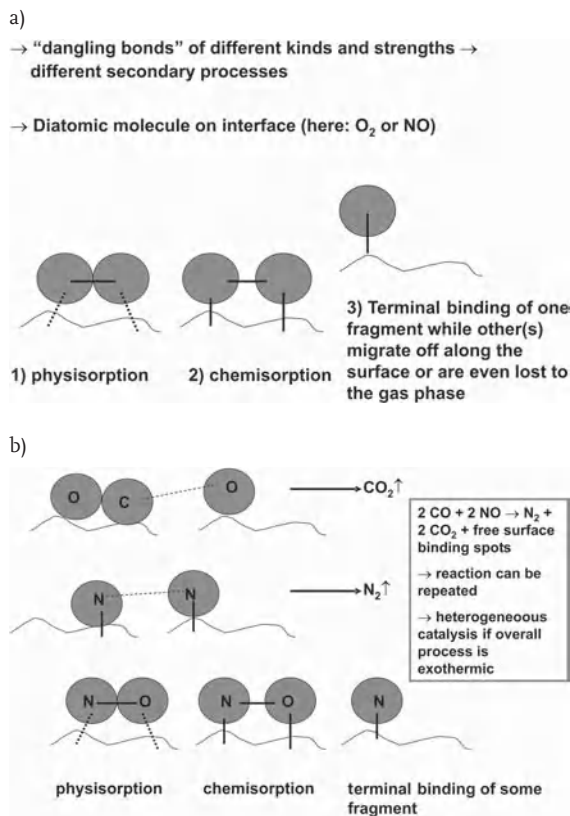


Figure 3.3 A sketch of the subsequent processes during physi-, chemisorptions and their relationship to heterogeneous catalysis. The reaction between NO and CO at some interface (a) produces the more stable and environmentally more benign products N₂

and CO₂ (b). The undulating lines are cross-sections through interfacial atoms (e.g., platinum). This particular reaction can also occur in the gas phase, producing most of the propulsion energy for gunpowder.

In some porous media small molecules (larger ones cannot do this for sterical reasons) may intrude into pores, that is, into cavities which itself have interfaces like those at the outside now along the pore fittings, that is, in small cavities inside the materials. The adsorption turns into absorption. Zeoliths, synthetic minerals (Figure 3.4), are capable of absorbing alkaline earth ions Mg²⁺, Ca²⁺, Sr²⁺ or those of many transition metals in their cavities which are dodecahedral.

The aluminosilicate backbone depicted in Figure 3.4 can also give away protons, from either hydroxyl groups bound to Al or absorbed water, for charge compensation, enhancing cation exchanger properties of the zeolith. This is pertinent to the activity of zeoliths in water softening when doing the laundry. Introduction of transition metal ions by either mere ion exchange or producing complexes inside

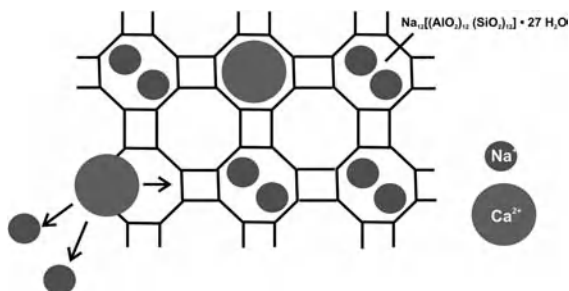


Figure 3.4 Internal structure of a zeolith, like zeolith standard mobile (oil) number 5 (ZSM-5).^{*} The sketch depicts the ion exchanger activity of this zeolith, replacing sodium ions by Ca^{2+} to “soften” water in which the zeolith was suspended (that is the reason zeoliths are added to laundry washing mixtures). The gray, clay-like residue you get after dissolving these detergent preparations in water actually is some kind of clay, exactly the zeolith grains). When other kinds of chemical reactions create larger particles inside some zeolith cavity, like polymerizations, precipitations of sulfides or selenides,

complex formation or that of large ion pairs or multiplets can block the way back to the solution. Hence ions which once got into such a cavity then will remain there. Zeoliths modified in this manner are important catalysts and photocatalysts (with chalcogenide or arsenide nanograins of well-defined size grown in the cavities until they fill them completely, absorbing radiation far redward of the absorption edge of the support and processing yet other substrates by electron or hole transfer co-adsorbed into still vacant cavities).

the cavities (with the ligands becoming co-adsorbed) can endow zeoliths with certain selective catalytic properties which are amply used in petrochemistry (oil refinery) but nowadays also in environmental chemistry.

In contrast, active carbon and similar organic sorbents usually lack both the propensity for ion exchange (except if prepared from pectin or rotten wood) and for chemisorptions but possess extremely large specific interfaces of sometimes

^{*} ZSM-5: the fifth in a series of synthetic zeoliths prepared by the above petrochemical company for its research purposes (Rothenberg, 2008). It is a so-called pentasil containing five-membered aluminosilicate rings. Unlike pure silica, some (<50%) of Si atoms are replaced in zeoliths and other aluminosilicates by (tri- rather than tetravalent) Al atoms producing excess charges to be compensated by cations, giving the general formula $M_y(Al; M')_xSi_xO_2$, where M is monovalent and M' is another trivalent ion once again replacing parts of Al, like Ga, Fe, Co, whilst Si may be partly replaced by Zr, Ti, or Hf (maintaining $y < x$, otherwise the

system gets unstable). In the latter cases, replacing M by protons provides extremely strong solid acids (“solid superacids”, HZSM5 and derivatives thereof; Staudte *et al.*, 2000) which attack even saturated hydrocarbons in the same way “magic acid” does (Olah, 1994). Thus carbocations and H_2 are formed, allowing synthesis of branched alcohols by water (or vapor) hydrolysis thereafter as well as reactions with other nucleophiles. Generally speaking, the mobility of the M ions renders zeoliths cation exchangers which is used in many ways.

$>1000 \text{ m}^2/\text{g}^{(4)}$ which render them excellently suited for binding organic compounds such as components of crude oil and other totally non-polar species (the active surface often is determined by gravimetry following adsorption of argon). However, moderately polar gases such as $\bullet\text{NO}_x$ and SO_2 are also readily adsorbed/absorbed by coke and other kinds of active carbon. When heating the material, they start reacting both with one another [lead chamber reaction; Equations (3.1) and (3.2)] and with parts of the carbon, producing dinitrogen while sulfuric acid⁵⁾ can either be eluted or released after more heating as SO_2 :



This is the active-coke method for coupled denitrification and desulfurizing flue gases. After drying the active coke thermally, the process can be repeated several times until the carbon is essentially consumed due to the reaction steps in Equations (3.3) and (3.4).

3.2.1.3 Immobilization

If substances get bound to sorbents with which they do react by chemical reactions, we are concerned with coupling reactions, often irreversible ones: halocarbons react with Fe or Zn sulfides to produce thiolates which remain in a bound state whereas highly halogenated compounds like CCl_4 and C_2Cl_6 are stripped of their halogens often without introduction of sulfur: hexachloroethane produces ethyne, ethane and some vinyl chloride at an FeS interface, that is, the C–C bond is not cleaved but neither tetrathiooxalate does form by simple exchange (Jeong and Hayes, 2003). If more noble metals are precipitated on more base ones like Fe in elemental state (cementation), this is another example of immobilization. For this case, see the case study on reactive walls (Section 4.3.1).

- 4) If you compare this to values of inorganic sorbents like zeoliths or other metal oxides (MgO , La_2O_3 , Al_2O_3 , silica), you must consider that densities of the latter are much higher, sometimes, like with Bi_2O_3 , an excellent sorbent for both organics and complexes thus used by one of the authors in sensitizing photochemical pollutant oxidations, up to some $10 \text{ g}/\text{cm}^3$. So apparently the specific surface of such a material is some six to ten times smaller than it would be comparing organic sorbent grains of identical particle sizes. In our hands, Bi_2O_3 samples ($\rho \approx 9.0 \text{ g}/\text{cm}^3$) with specific surfaces of but $1\text{--}2 \text{ m}^2/\text{g}$, thus comparable to organic sorbents of about $10 \text{ m}^2/\text{g}$, performed quite well in adsorption-based photocatalysis.
- 5) Being an extremely polar liquid, sulfuric acid does but weakly adsorb to the completely non-polar active carbon (active coke); the same holds for water (or HCN, HF when cleaning toxic gas or fume mixtures. Hence gas masks which are to protect against these gases must contain sorbents other than active carbon, at least in addition). H_2SO_4 starts to act as a considerably strong oxidant (much like nitric acid) only at $T > 230^\circ\text{C}$.

Biogenic materials like peat (Romão *et al.*, 2007) or lignite (Fei *et al.*, 2006; Qi *et al.*, 2011) contain many functional groups which can withhold heavy metal ions by complexation, with their solid and polymeric structure causing immobilization once again, besides ion exchanger properties, like carboxylate, phenolate, enolate, or 3-ketoenolate groups (Romão *et al.*, 2007; Blume, 1992). Lignite (and flue ash after its combustion) contain rather many heavy metals in substantial amounts (Mn, V, Ni, Ge, Cd, Hg) which mainly made their way into the fuel by this combination of complexation and ion exchange rather than being derived from the biomass lignite or peat were derived from (for metal levels in peat-forming *Sphagnum* mosses, see Markert, 1996).

3.2.2

Redox Potentials, Pourbaix Diagrams and Speciation

In a solution (either aqueous or organic) an element or its stable speciation form does interact with its environment (solvation sphere) to a considerable extent, and this interaction in turn does determine its behavior. If the conditions in the immediate surroundings of this element (-compound, -ion) are varied, the “embedded” (“solvated”) element may respond by undergoing reactions which then will often include solvent molecules or parts thereof (e.g., after deprotonation of solvent). The “outer surface” of any atom, ion or molecule consists of its outer electrons inevitably,⁶⁾ and it is only this outer shell of electrons which takes part in chemical reactions (this need not mean the uppermost orbitals only but can involve lower ones in transition or f-block metal ions also when these undergo thorough oxidation or become bound to ligands). Accordingly, this outer shell of electrons can respond to challenges by its environment (offering yet more free electrons or trying to remove some to oxidants around) in different ways, either getting filled up by binding other chemical species such as molecules (e.g., NH_3 or the solvent itself) or (quite usually an-)ions, or losing electrons if the “gas pressure” of electrons is too low nearby to maintain and stabilize the present state of matter(s). This “gas pressure” of electrons is a chemical potential, and any chemical potential which involves charged particles (electrons) also is or corresponds to an electrical potential. Although it cannot be determined in absolute values but must be related (compared) to that of some standard reaction, it is called redox (*reduction/oxidation*) potential accordingly. This latter term refers to the balance between forward and backward reactions which is typical of any chemical equilibrium state.

Both the influences of electron potential and of solvent interactions which may cause hydrolysis or precipitations of hydroxides can be jointly depicted in some

6) This also holds for the proton in condensed media: there is no “ H^+ ” whatsoever but always species in which the proton is linked to some solvent molecule and thus “buried” under the electron cover of the solvent molecule, forming H_3O^+ in water or species such as H_2F^+ or $\text{H}_2\text{SO}_3\text{F}^+$ even in superacidic media where one might

presume free protons to lurk around given the extreme protonation abilities of these—usually rather viscous (association of protons in long chains of anions!)-media. Any other chemical species that $\text{H}(\text{I})$ has at least a pair of 1s electrons around its nucleus (Li^+ , Be^{2+}).

pH/Eh diagram which also is called a Pourbaix diagram in honor and memory of that Belgian chemist (Marcel Pourbaix; 1904–1998) who designed them.⁷⁾ Insofar as these are or contain aqueous media or (sub-)phases also, environmental compartments [viz., the (thermodynamically stable) states of the elements contained in them] can also be described by Pourbaix diagrams, even with some spatial resolution. Since different speciation forms also (often vastly) differ with respect to all toxicity, solubility and bioavailability, data from Pourbaix diagrams can be used to find out how to treat “simple” and “mixed” (multielement) contaminations in order to minimize toxic exposition of man, animals and food. However, note that Pourbaix diagrams take regard of those speciation forms only which are thermodynamically stable in some region of the (theoretical) aqueous diagram, and there are common and hazardous forms of chemical elements we are concerned with in environmental chemistry which are either labile toward disproportionation (e.g., SO_2 which decomposes into sulfur and HSO_4^- catalyzed by, e.g., elemental selenium) or even capable of decomposing into their elements, like oxides of nitrogen or chlorine. Such species are not covered by the merely thermodynamic Pourbaix approach, whereas their removal is just a matter of appropriate catalysts and reaction partners rather than controlling redox and pH levels appropriately. Yet in either case one must try to “adjust” chemical conditions in a way as to minimize the main hazards.

Generally speaking, chemical elements will interact with their surroundings whatever its structure and state are. Hence they will undergo a multitude of chemical reactions in all the environmental compartments and also in biomasses which are highly heterogeneous with respect to both pH and Eh. For example, by passing through the gut of some vertebrates including humans, pH varies from 1.5 (stomach) to slightly alkaline while Eh varies from fully oxidic (mouth, throat) to sometimes the onset of sulfate reduction. Now superpose the Pourbaix diagram of some almost arbitrary non- or transition metal to see what will happen within this range of parameters. There will be fractionation among the environmental compartments and biomass along these chemical (and sometimes, thermal) gradients especially if either hardly volatile or ionic forms are produced or some part of the element is going to be converted into gas or vapor (e.g., $\text{NO}_3^- \rightarrow \text{N}_2$ in air) besides precipitation (except with nitrates, acetates) and adsorption processes.

Many processes and purification/sanitation protocols in environmental engineering draw upon such effects of fractionation and disproportionation. With their being redox processes, redox speciation must be “run” in appropriate conditions of both pH and Eh. Apart from thermodynamics, sometimes such reactions will take place at a reasonable rate only if pH is such that surfaces are constantly “cleaned” or etched or ligands must be added to remove some products or induce

7) Originally, just before World War II, the issue to be tackled by these diagrams was just the corrosion of metal alloys (when will an oxide cover form to stay and protect to underneath bulk metal or alloy?). Pourbaix diagrams were introduced into geo- and

cosmochemistry only much later (Garrels and Christ, 1965), and their potential uses in environmental chemistry and technology has, from our point of view, still not been adequately appreciated till now.

the reaction altogether. Pourbaix diagrams are rather important but only some part of the story; for example, an iron-based rusty wall will provide efficient and fast reduction of chromate(VI)–which is feasible all over the pH range from highly acidic to staunchly alkaline in thermodynamic terms–only in some small region around pH 11.

Of course, one should be reminded that reduction of chromate is a prime example for detoxification by redox speciation. As interfaces and chemical gradients can also be introduced into air, for example, with UV-illuminated titania interfaces which both adsorb organic vapors and release OH radicals in light, chemical gradients can also be prepared in air, like in water or soil. However, the outcome is not always benign (i.e., mineralization of pollutants, reduction of NO_x) but can also give rise to unwanted secondary compounds. Figure 3.5 shows this effect in a sketch and in an experimental setup.

Living conditions of other organisms are touched by chemical speciation, transport conditions (e.g., formation of volatile or lipophilic forms readily exhaled or accumulating in lipid tissues) and secondary compounds in either soil or water. Mobile products can carry over to affect neighboring biocenoses across ecotones: wet deep soil layers rapidly become anoxic and give rise to CH_4 and H_2S which create damage in tree rhizosphere if they ascend up to the roots (there are only specialized trees which cope with anoxic soil or sludge conditions by passing air into the soil just through hollow roots, e.g., alders or mangroves). Biomethylated species produced by moulds are sometimes sufficiently stable for transport but

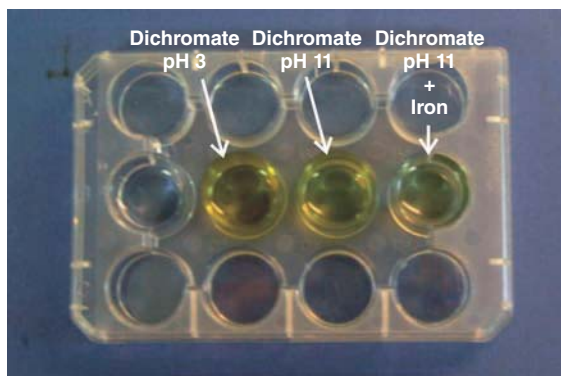


Figure 3.5 Chromate reduction by iron rusty walls. The outcome of a model experiment on chromate reduction by iron filings. The “bleaching” of strongly yellow-colored solutions upon contact with Fe alone does not prove Cr(VI) sanitation as Cr(VI) has some pH indicator properties, changing colors from light orange $\text{Cr}_2\text{O}_7^{2-}$ in acidic media to less intensely colored alkaline CrO_4^{2-} solutions. This is seen here also:

neither the left nor the central sample underwent reduction but represent appearances at pH = 3 and pH = 11, respectively, while the right one was obtained by reducing an aliquot of the central one at constant pH 11. Here, bleaching actually refers to reduction. Though long black needles were produced as a by-product, these were not ferromagnetic, excluding formation of magnetite.

can also pass intact skin even of mammals.⁸⁾ Soil-dwellers with soft, wet skins without a ceratinous layer are more exposed, also to heavy metals. Among earthworms, nematodes or amphibians like cecilians which all have skins very easy to be penetrated by chemicals, some earthworms of genus *Lumbricus* are adapted to deal with compounds and ions absorbed through skin or released by polymer degradation in the guts: *L. rubellus* will accumulate them in the body but in the same turn can detoxify them by producing solid, insoluble sulfide particles. With these sulfides being often intensely colored, this worm which otherwise is lightly pink will attend the typical color of the corresponding sulfide ["don't eat yellow worms" (yellow-orange sulfides: cadmium or arsenic; Jander and Blasius, 1978)]: this is a highly uncommon manner of bioindication which also is uncommon in biochemical terms as sulfide particle formation inside cells hitherto was observed only in certain kinds of yeast rather than multicellular eukaryotes before.

All these three parameters (electron density, pH value, chemical binding) may vary. The chemical environment which is most common on Earth and most relevant to environmental chemistry also is liquid water. Depending on the kind and chemical properties of an element, it might respond to single ones or all three of these parameters by changing chemical speciation forms. An iron(III) ion will first become "wrapped" by a shell of water molecules to produce hexaquairon(III) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ when some oxidized iron salt is dissolved in water. The following discussion of later changes will assume only this hydrated state of Fe^{3+} ion as the starting point. Let us now have an actual consideration of what will happen to $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ if exposed to the three kinds of transformations (A, B, C in Figure 3.6):

- A) If the "electron density" is increased in the aqueous solution, by adding reducing ions or compounds such as iodide, $\text{Fe}(\text{III})$ will eventually take up an electron to form Fe^{2+} . Conversely, when electron activities are diminished so much that water also gets unstable, and high $\text{pH}^{9)}$ $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ can give away yet more electrons to yield ferrate(VI) $[\text{FeO}_4]^{2-}$ which is dark blue and resembles the structure of chromate.
- B) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ can react with donor (ligand) ions like chloride or thiocyanate to form complexes like tetrachloroferrate(III) $[\text{FeCl}_4]^-$ or thiocyanatoiron(III) ion $[\text{Fe}(\text{SCN})_{\text{aq}}]^{2+}$ (red).
- C) If the solution is made less acidic than about pH 2.5, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ first loses a proton to afford the photochemically active hydroxoiron(III) ion $[\text{Fe}(\text{OH})_{\text{aq}}]^{2+}$, then iron(III) oxide Fe_2O_3 is precipitated.

8) Remember the tragic death of United States toxicologist Karen Wetterhahn (1947–1995) who died from spilling dimethyl mercury over her hand in a damaged laboratory glove. The $(\text{CH}_3)_2\text{Hg}$ was absorbed transdermally into the central nervous system (CNS) to such an extent that it killed her after a prolonged coma several months later.

9) In neutral or acidic solutions water is rapidly oxidized by ferrate which also can oxidize both Mn or I into the heptavalent states. Because it does degrade organic contaminants completely also while forming innocuous Fe_2O_3 , ferrate(VI) was tried as a reagent in cleaning wet soils [Anonymous (with Battelle Institute), 2007].

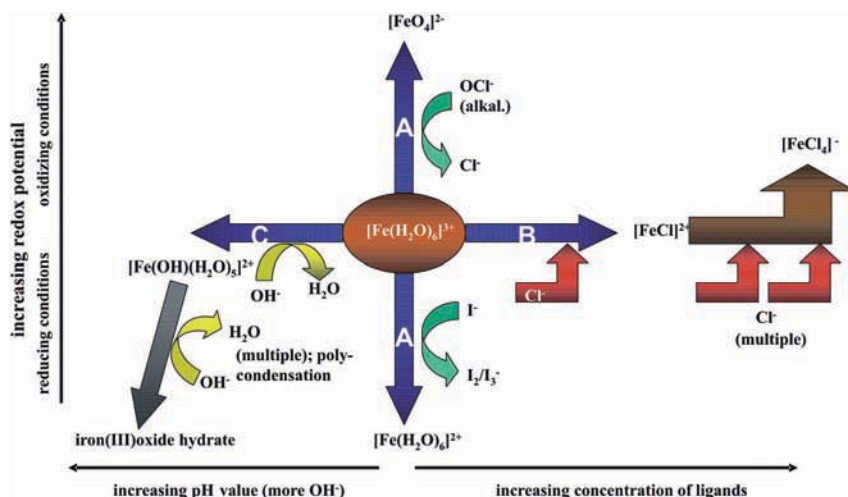


Figure 3.6 Reactions which an iron(III) aquaion undergoes if the “environmental” conditions pH or Eh are changed. A: redox processes. B: complexation. C: hydrolysis and eventual precipitation of oxides. Hypochlorite OCl^- is an oxidizing agent and iodide a

reducing one, whereas chloride ions add to $\text{Fe}(\text{III})$ without a redox process tend rather to yield $[\text{FeCl}_4]^-$ in the end, and hydroxide (base) addition causes hydrated oxides to separate.

All of these processes are reversible; thus, forward and backward reactions (hydrolysis of complexes, dissolution of oxides upon acid addition) compete to construct some equilibrium state eventually. This equilibrium constant is given by the ratio of “forward” and “backward” kinetics or in thermodynamic terms (free energy ΔG). With pH value and redox potential set, it should be feasible to identify the iron species which are present here, while the process of establishing this equilibrium is called speciation. Thermodynamically stable¹⁰⁾ speciation forms can be depicted to depend on pH (ordinate axis) and Eh (abscissa). Hence such diagrams are called pH/Eh or Pourbaix diagrams. Formerly used to better understand corrosion of metal alloys, nowadays such diagrams are available for most elements, often covering elevated temperatures up to 1000°C ¹¹⁾ and phases which besides O, H and the respective elements also contain C, P, S, Cl and so on.

10) See above for formation of compounds or ions which are highly significant to environmental protection and technology but do not show up in Pourbaix diagrams simply because there is no region where these are thermodynamically stable, like SO_2 , NO_2^- or most organic compounds (the thermodynamically stable pure CH species will be methane, but neither unsaturated nor aromatic compounds, for example: $2 \text{C}_6\text{H}_6 \rightarrow 3 \text{CH}_4 + 9 \text{C}$; $\Delta G = 410.0 \text{ kJ/mol}$; calculated from

thermodynamic data in *CRC Handbook of Chemistry and Physics*; Haynes and Lide, 2010).

11) In technical (environmental) chemistry this refers, for example, to combustion processes, allowing for unsaturated and even free radical hydrocarbons and formations of highly toxic products like CO, HCN while in geochemistry processes in volcanoes are to be tackled by such modified Pourbaix diagrams.

Solid precipitates made of carbonates, phosphates or sulfides (that is, classical Pourbaix + C, P or S, respectively) will not only influence corrosion [formation of vivianite $\text{FePO}_4 \cdot n\text{H}_2\text{O}$ by phosphoric acid treatment (and be it immersion into Coca-Cola) will thoroughly reduce iron corrosion] but, being most insoluble, also compromise bioavailability of such metals. In turn, microorganisms which otherwise could remove some organic pollutants might not grow and reproduce for lack of some essential element if a precipitating agent is there around, while element toxicity, of course, is also affected by speciation. If there are toxicity data for the different pertinent speciation forms¹²⁾ of an element and these are all thermodynamically stable in some pH, Eh parameter pair (range¹³⁾), the proper conditions can be identified to minimize toxicity or cleave a dissolved or vapor nuisance by precipitating (or co-precipitating, starting with trace amounts along substantial excesses of a chemically similar but less harming compound).

Another, environmentally and toxicologically most eminent example for redox processes in environmental chemistry which can be accounted for by superposition of Pourbaix diagrams, are the tragic chronic As mass poisonings in Bangladesh, nearby border regions in both Burma (Myanmar) and India (State of Western Bengal) and also certain other river mound regions, for example, the Red River in Vietnam. As already mentioned, oxidation states of As which can occur in the environment differ vastly with respect to toxicity, inorganic As(III) being much more toxic than arsenate(V) which, moreover, can be included in insoluble salts, or than organo-As compounds.¹⁴⁾ Chronical arsenic poisoning first causes changes

- 12) This argument can cover, once again, only the thermodynamically stable forms of speciation, excluding, for example, nitrite. If one needs to know what will happen to some dissolved pollutant which lacks a thermodynamic stability region of its own, whether it is going to vanish in a given mixture, you must look upon redox potential tables. For soil solutions, the actual existence regions of fully oxidized forms of some element [O, N, Fe, S, C, and H, respectively, plus mixed Mn(III;IV) 14) oxides] can be deduced from empirical lists (e.g., Scheffer *et al.*, 2002) which will, moreover, reveal some "sluggishness" (poor kinetics) or—withstanding the efficiency of redox enzymes like nitrate or sulfate reductases—activation barriers allowing the above oxidized forms still to persist at rather negative potentials. This is done by comparing to formally expected transition potentials; difference may be as large as 200–300 mV.
- 13) Be prepared for surprises: the carbon-added iron Pourbaix diagram at room temperature or 100 °C does contain harmless FeO phases like magnetite (no C) plus likewise innocuous siderite FeCO_3 and schreibersite Fe_3C (no O) but in between, stably coexisting with either of the latter two + CO_2 , there is also volatile, highly toxic iron pentacarbonyl $[\text{Fe}(\text{CO})_5]$ which is actually produced in closed landfills. The sulfur-added C Pourbaix diagram is most sensitive toward temperature: at room temperature CH_4 and SO_4^{2-} will stably coexist, producing an explosion hazard at worst while in boiling water the stable species to coexist are CO_2 or HCO_3^- and stinking, highly toxic H_2S . According to both European Union and United States norms, the acceptable total As level in potable water is $\leq 10 \mu\text{g/l}$ (some 130 nM). Some organisms are capable to produce speciation forms even more toxic than As_2O_3 in anaerobic conditions, namely arsane AsH_3 or monoalkyl arsines R-AsH_2 , which are gaseous but—luckily—do not persist in air for long. Nevertheless there are cases of arsane poisoning, including fatal ones (inhalation of AsH_3 may stop heartbeat immediately and, very much like H_2Se , may bring about hemolysis), due to both microbial activity and improper material uses (aluminum claddings of wells which reduce As dissolved in water all the way into AsH_3).



Figure 3.7 Skin tumors on feet, caused by chronical uptake of arsenic by drinking water and rice consumption. Courtesy: www.uni-karlsruhe.de/~img.

in the skin structure at the lower surfaces of hand and foot (Figure 3.7), often turning into deep-rooted malign tumors. In later stages, these carcinomas will cause the loss of single fingers or toes nearby or even necessitate the amputation of hands or feet. Metastases may also occur.

When drilling wells for drinking and irrigation water supplies in Bangladesh—most of this country being nothing but the common deltas of the Rivers Ganges and Brahmaputra—fluvial sand layers were penetrated, the typical depths of these wells being some 35–40 m. These sands contain lots of organic sediment from the River Ganges especially which form “pockets” to be buried deep under the regions where oxygen gets to sooner or later. By erosion of the Himalaya mountain cliffs, substantial inorganic compounds—including some arsenic—are washed down both the Upper Ganges in Nepal (Southern Himals) and the Tsangpo in Tibet (Northern Himalayas) which is going to become the River Brahmaputra

in its lower parts (Sikkim, India, Bangladesh). Of course, if adsorbed onto sediments, such compounds, be they poisonous or not, become also locked up in the sands of the delta, and if one starts pumping water, both the sandy matter and organic pocket inclusions will be subjected to horizontal water flows refilling the sediment pores around the well, and this will occur much below the oxygenated regions of the sediment column, with nitrate or sulfate also being scarce in this particular case. The upper sediment layers will be periodically relocated by catastrophic floods in the delta which took many thousands of lives in Bangladesh and Burma during the last decades but rather reduce oxidant access to deeper sediment layers as these become more compact. The water replenishing the well fillings is anoxic, and it passes regions where there are oxidizable organic materials.

Hence local microorganisms will use much weaker oxidants to process ambient organic C than O_2 , with arsenate being about the strongest oxidant locally available, its potential placed in between that of $MnO_{2-\delta}$ (manganite, birnessite) and of sulfate. When passing a certain redox potential level in soils, there will neither abrupt onset of some reduction take place, let alone completion of this process before long, rather, reductions of oxidants which have similar redox potentials under soil liquid conditions, like Fe(III) and Mn oxides or arsenate and sulfate, occur partially side by side although they are effected by different oxidoreductase enzymes. Luckily, S commonly is far more abundant than As, causing As(III) to be precipitated as As sulfide mixture by H_2S forming parallel. This sulfide mixture contains some species with As–As bonds and ternary M(etal) thioarsenates besides the simple sulfide As_2S_3 , all of them being both extremely hardly soluble in water and fairly abundant minerals. Given there was an excess of sulfate, the water in the wells will be kept free of As even if some pocket containing organic matter was hit by drilling the well. Matters change dramatically if sulfate is (almost) absent: then As(III) gets dissolved in concentrations of up to 3 mg/l (!; 300 times the limiting value for drinking water). Even worse, it is going to be enriched yet more by rice plants if these are irrigated. As the pockets of organic matter some 35 m deep in the underground are scattered here and there, there is just a statistical chance of hitting such pockets; accordingly, every single well has to be checked for arsenic. Two wells located in the same backyard, less than 10 m apart, may differ in water As levels by some factor of 50 or even more.

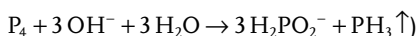
In water just a certain range of conditions may be realized: it can become reduced (to yield H_2) or oxidized (to yield O_2) even though much stronger reductants than H_2 (e.g., boranates BH_3X^- , $X = H$, alkyl, CN or OR', M^{2+} ions for $M = V$, Cr, Eu, Yb) or oxidants more electron-withdrawing than O_2 [peroxodisulfate, Ce(IV), MnO_4^- , $XeF_2^{15)}$] may persist for quite a while in cold water, and solutions cannot be made arbitrarily strongly protonating (acidic) or deprotonating (alkalinic), both parameter ranges being considerably smaller in H_2O than in some

15) Permanganate can be made to release dioxygen, for example, by adding BF_3 in CH_3CN , and XeF_2 is—besides OH radical—the strongest oxidant in the

ground state (rather than photogenerated) which is actually tractable in water at its $E^\circ/2 \approx 2.6$ V versus NHE (normal hydrogen electrode; pH = 0).

other solvents. Accordingly it cannot be anticipated that all the elements other than O, H will respond to changing conditions in water by displaying all three kinds of reactions denoted by (A), (B) and (C) in Figure 3.6. To mention an extreme case, alkali metal ions form just very weak complexes and undergo neither of the other reactions in water; thus, the only speciation form to be observed will be the aquated M^+ ion. Things are quite different in other solvents: there are alkalide (alkali metal anions) M^- ($M = Na$, less so with K or Rb) in amine solvents, and complexation will also occur in acetonitrile (Li) or sulfoxides.

To start with a simple example, let us consider the Pourbaix diagram of *cadmium* (Cd, Figure 3.8a). Cd^{2+} can be just barely reduced to the metal in aqueous media,¹⁶⁾ and it forms some complexes. In alkaline solutions $Cd(OH)_2$ will be precipitated to re-dissolve as tetrahydroxocadmiate $[Cd(OH)_4]^{2-}$ in very high pH media. Non-metals often readily react with the components of water in similar conditions and covalently add H and OH, when undergoing redox reaction (disproportionation, e.g., of white phosphorus according to:



Another example, now forming a Pourbaix diagram which is a little bit more complicated, is *sulfur* (Figure 3.8b). H addition after reduction affords H_2S (lower left part of diagram) while OH addition and deprotonation after an oxidation give rise to sulfate (upper part, center). However, non-metals do not readily form complexes with typical ligands present in the environment like humic or amino acids, except for halides. Other elements, like vanadium or plutonium, undergo all three kinds of processes during speciation to yield so many stable and metastable species that the Pourbaix diagram is going to cover literally dozens of—correspondingly small—stability regions. In addition, V, Pu and several other metals undergo polymerization (olation) reactions.

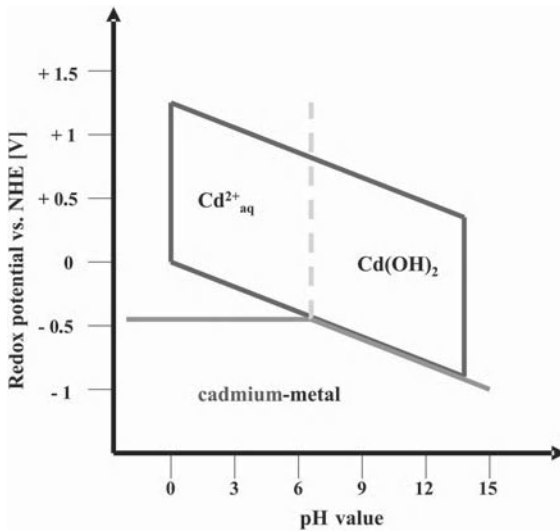
Concerning Figure 3.8b, it is conspicuous that there are just three different species except for protolysis, omitting peroxodisulfate¹⁷⁾ which is thermodynamically stable only at so high potentials that it need not be considered in environmental chemistry except perhaps as an environmentally benign oxidant: elemental sulfur, sulfate(VI) and sulfide or H_2S . Accordingly, there are just two stable oxidation states other than the element, namely, $-II$ (sulfide) and $+VI$ (sulfate) which, by the way, also holds for peroxodisulfate. As we noticed before, many other familiar compounds like SO_2 and its hydrated forms, thiosulfate or polysulfides will not show up in a Pourbaix diagram because they are metastable

16) The classical Ni/Cd accumulator would not be rechargeable if it were impossible to precipitate Cd by electrochemical means from aqueous alkaline solutions. This does easily succeed because there is substantial overvoltage for H_2 formation at a Cd cathode (about 1 V, even larger than with mercury).

17) Even though its potential is very high, peroxodisulfates with NH_4^+ or organic

counter-ions are kinetically very stable; unlike perchlorates, such peroxodisulfates are no explosives. Oxidation of organics by $S_2O_8^{2-}$ requires some one-electron redox agent as a catalyst like Ce(III) or Ag^+ . Actually peroxodisulfate is the most strongly oxidizing closed-shell chemical species (disregarding radicals like OH) to exist in water except for certain noble gas (Xe) compounds and ions.

a)



b)

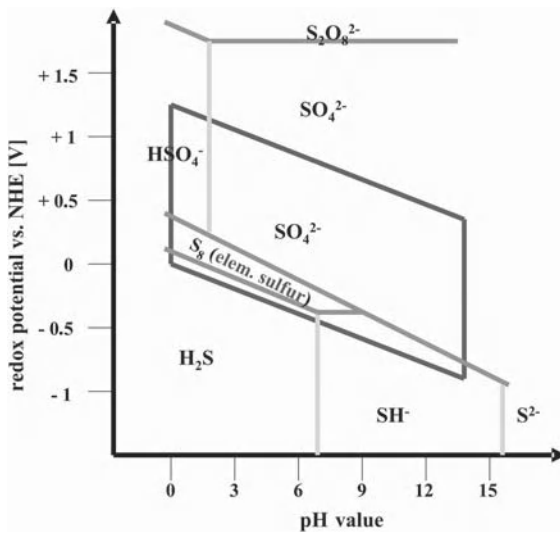


Figure 3.8 Two rather comprehensible Pourbaix diagrams, those of cadmium (a) and sulfur (b). Although the redox transition line cadmium/ $\text{Cd}(\text{OH})_2$ is located somewhat below the lower stability edge of water (i.e., hydrogen release), the overvoltage blocking actual H_2 production on Cd is so large that

Cd metal becomes kinetically stable. For sulfur (b), note the superposition of redox and protolytic transformations and the fact that (colloidal, disperse) elemental sulfur is stable only in a small potential region in neutral or acidic solutions.

at best in all aqueous conditions. This is not a “failure” or disadvantage of the description; rather this is to say that its—obviously exergonic—decay occurs by disproportionation into S_8 [= elemental (octa-)sulfur] and sulfate and might even be catalyzed,¹⁸⁾ removing this pollutant more quickly. The appropriate catalyst is selenium, while polysulfides or thiosulfate also undergo disproportionation releasing elemental sulfur in acidic media [whereas polysulfanes H_2S_x ($x = 2$ to several dozens) may be prepared by passing H_2S through molten sulfur, acidification of S_x^{2-} solutions will only afford colloidal sulfur + H_2S]. Accordingly, compounds or ions which are “hidden” from the thermodynamic diagram just thereby reveal their chemical vulnerability, prompting us to look for an appropriate catalyst which turns them into the (more) stable speciation forms. Temperature effects can be tackled by considering Pourbaix diagrams for other T values while inclusion of fourth and so on elements E' besides E, O, and H addresses shifts and by-products. To give a practical example, consider what happens when NO_x , SO_2 (both “hidden” in the diagrams and, accordingly, less stable than nitric and sulfuric acids, respectively) plus water vapor get adsorbed to coke in flue gas purification (i.e., $E' = C$). The superposition of diagrams then straightforwardly reveals that both hazardous oxides are going to be reduced to the respective elements, with CO_2 being the by-product. Kinetics is another matter, of course, thus often calling for catalysis. “Catalysis” may also translate into “biocatalysis”, with certain enzymes doing tricks like methane CH_4 activation or N_2 reduction hitherto hardly mimicked by man under “moderate” conditions (Rolff and Tuzcek, 2008). As there is still thermodynamic control, hence Pourbaix diagrams also apply to bio- and bioinorganic chemistry, and thermodynamic control is most typical of biochemistry exactly for the efficiency of enzyme catalysts (Fränzle, 2010; Wolfenden and Snyder, 2001), biotechnology can be understood, designed and applied by the same principles.

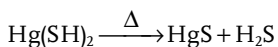
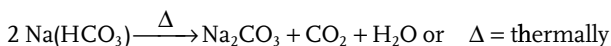
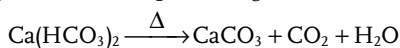
In neutral or alkaline solutions, direct reduction of sulfate into sulfide S will take but moderately negative potentials, then cleaving heavy metal ions from solution or suspension (suspended sludge) by sulfide precipitation. Since this would occur in a digestion tank also, some part of heavy metals must be precipitated before by alkali additions [usually, $Ca(OH)_2$] to limit the heavy metal freight (Cd, Pb, Hg, etc.) in fouled sewage sludge. H_2S is much weaker an acid than sulfuric acid, and SH^- , unlike HSO_4^- will not behave as an acid in water at all (cf. vertical yellow lines in the Pourbaix diagram of S, Figure 3.8b). Controlled anoxic conditions can be used to “de-acidify” deeper layers of water bodies such as lakes by

18) This is an acid-catalyzed clock reaction with selenosulfate $Se-SO_3^{2-}$ intermediate produced from sulfite and elemental selenium. Se_8 does act as an efficient catalyst also in oxidations of alkenes by $OHal^-$ (Sykes, 1977), isocyanides by sulfur (Fujiwara and Tsutomu, 1991) to yield “mustard oils” R-NCS eventually. The reaction does proceed by continuous reoxidation of H_2Se by sulfur and SO_2

producing H_2SO_4 which enhances reaction speed steadily for the mixture gets ever more acidic (sulfuric acid product is an acid catalyst), with disproportionation of S(IV) being terminated by precipitation of a mixture of elemental sulfur and selenium, making the solution suddenly and rapidly turbid after a while (hours to days: *clock reaction*).

pumping the water and contacting it to organic reductants such as straw. bacteria then are a catalyst of S reduction while sulfate¹⁹⁾ otherwise is a kinetically poor oxidant below some 200 °C.

Rather than reacting with hydroxide ions or water, low oxidation states of non- and semimetals can react with protons to produce hydrides which are rather volatile, thermally unstable and highly toxic, like arsane AsH₃. This is another (second) pathway into redox-induced hydrolysis, protonation following to multiple²⁰⁾ electron uptake rather than starting by oxidation of the element. This also holds for sulfur where H₂S in acids, SH⁻ in neutral or alkaline solutions dominate the areas of low redox potentials; owing to its Brønsted basicity, you will not find “genuine” sulfide in protic solvents like water or alcohols. Formation and precipitation of sulfides occurs by secondary condensations in hydrosulfides, quite similar to hydrogen carbonates producing carbonates, CO₂ and water upon heating:



Elemental sulfur is stable only if pH < 8, some behavior which is quite typical of non-metals which form stable hydrides [H₂S is an exothermic (!) compound]. Thus, there will be disproportionation in alkaline media—which is very slow with S—in the heavier halogens Cl, Br and I and in white phosphorus P₄, yielding the corresponding hydrides or their anions (halide) together with oxoanions of intermediate oxidation states like halogenate(V) HalO₃⁻ or phosphinate H₂PO₂⁻²¹⁾

- 19) Biogenic (all bacterial, plant and animal) sulfate reductions use a trick which also permits PH₃, AsH₃ formations in strongly anaerobic conditions: rather than trying to transfer H atoms, molecules, hydride ions or electrons to SO₄²⁻ directly, the latter is phosphorylated first to yield phosphosulfate with an excellent leaving group (H₂S₂O₇, chloro- and bromosulfonic acids all are far better, faster oxidants than H₂SO₄ for the same reason), to be reduced by hydride transfer (pyridoxamine) and ferredoxin-based electron transfer only thereafter.
- 20) Mono- or divalent cations will undergo hydrolysis in strongly alkaline media (very high pH) if at all, rather hydroxides will be precipitated. Further, trivalent ions [Fe(III), Ru(III), Al] hydrolyze (give away protons) in rather acidic solutions already, and tetravalent or even higher-charged cations will not exist in water (neither in other solvents) as M⁴⁺ ions but form [M(OH)]³⁺ (Th) or MO²⁺ (vanadium, zirconium), at best. By forming hydroxo- or oxobridges, corresponding cations form long chains of coordination polymers (olation), which often behave like di- or trivalent ions with respect to formation of insoluble salts.
- 21) With P and Cl, disproportionation will not provide that speciation state which is stable in thermodynamic terms (i.e., perchlorate ClO₄⁻ or phosphonate HPO₃²⁻) but will come to an end before at room temperature, namely with chlorate and phosphinate. According to their Pourbaix diagrams yet other non-metals could undergo disproportionation, including tellurium to afford ditelluride Te₂²⁻ and tellurite(IV) TeO₃²⁻ but only if exposed to really concentrated alkali hydroxide brines (pH >> 14) while selenium cannot even then do so. Germanium is known for long to react with alkali, starting from GeO or Ge(OH)₂ to produce yellow polymeric compound mixtures with Ge-H bonds which, unlike simple germanes Ge_xH_{2x+2} will spontaneously ignite in air.

[halogene(V) or P(I), respectively]. Limiting conditions for such reactions are triple points in the Pourbaix diagram where three different speciation forms can co-exist (which is the maximum in a single phase²²⁾). These are sharp triangles in the diagram. Analogous reactions are seen in metals also, but omitting negative oxidation states in favor of intermediate ones.

When there are no appropriate ligands, the strong oxidant $\text{Mn}^{3+}_{\text{aq}}$ which nevertheless is fairly stable in acidic media will decompose at $\text{pH} > 3$ into Mn^{2+} and $\text{Mn}^{\text{IV}}\text{O}_2$. In contrast, green manganate(VI) $[\text{MnO}_4]^{2-}$ is stable in very alkaline media but will disproportionate to afford violet permanganate MnO_4^- and MnO_2 once again. The direction of these reactions will be inverted in acidic media (com- or synproportionation rather than disproportionation): passing H_2S through an acidic sulfite solution (or conc. H_2SO_4) will afford sulfur or polythionates (Wack-enroder's liquor) while the corresponding reaction in the chlorine system might really run dangerous: if you pour hydrochloric acid to a solution of chlorate-based WC cleaner, violent evolution of chlorine will occur! Statements from the Pourbaix diagram thus might directly affect your occupational safety, and the chances to clean up environmental damages. It can be planned to precipitate insoluble or less toxic forms of some element in a given milieu by manipulating the latter or produce a contact which changes redox potentials (rusty wall) or pH (liming). Yet you will rarely be so successful as to accomplish satisfying purification for all the "noxious" elements around.

Though kinetics are not an issue covered by Pourbaix diagrams, they are significant both in corrosion theory and environmental engineering for running or avoiding certain processes:

It is obvious from the Pourbaix that in all the pertinent regions of pH and redox potential of base metals such as Be, Al, Ti, Zr, Nb or Ta only oxides and hydroxometallates – not the metals! – are stable, implies that these metals – and their alloys like Zircalloy in nuclear technology – can be applied in contact with aqueous media only if oxide or aquoxide layers on the metals are stable. In strongly alkaline solutions all these metals will dissolve forming ions such as tetrahydroxometallates $[\text{Be}(\text{OH})_4]^{2-}$ or $[\text{Al}(\text{OH})_4]^-$ or hexaniobate $[\text{Nb}_6\text{O}_{17}]^{4-}$ when stability regions of (often amphoteric) oxides are terminated by higher pH. If the oxides remain insoluble in rather acidic solutions (Nb, Ta,²³⁾ Zr) the metals resist attack by acids even though they could release H_2 from H_3O^+ .

22) For example, when dissolved (cp. Fränzle, 2010 for biochemical implications; Wedler, 1982). If there are separate phases, for example, solid unsoluble (aqu-) oxides, immiscible liquid phases (CCl_4 , iron pentacarbonyl) or gaseous hydrides, even more different speciation forms of some element might co-exist also in the Pourbaix diagram. This means that a redox reaction – also other than disproportionation – might not be driven to completion by removing one of the speciation forms continuously or by

changing concentration levels or temperature.

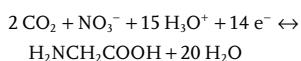
23) The fact that its oxide would not dissolve in acids (other than aqueous HF) was the reason why tantalum was given its name, to remind of mythological Greek (of Phrygia, Asia Minor) king Tantalos who was punished by the Gods by being kept from drinking however thirsty he was. Likewise Ta_2O_5 will not take up protons ("drink") to form any cation in acidic solutions. The homologous (Group 5b: V, Nb, Ta, Db) niobium (Nb) the oxide of

Another interesting case in environmental chemistry and biotechnology is the Pourbaix diagram of carbon, including N atoms. It reveals that any more complicated structure (C_{2+x} molecule or even CH_3OH , $HCOOH$) in organic chemistry will be unstable with respect to both CO_2 or of HCO_3^- and of CH_4 ; hence along the separation line of stability regions of CO_2 or of HCO_3^- and of CH_4 such molecules can possibly undergo disproportionation releasing energy. Free energy gains (in biochemistry: ATP) from this disproportionation can suffice to support the entire catabolic metabolism, for example, of clostridia (which, moreover, produce both molecular hydrogen thereby and sometimes extremely toxic byproducts such as Botulinus toxin). Much of environmental biotechnology draws upon such thermodynamic features, including methane formation in sewage digestion tanks, with “biogas” being actually the final residue of the above disproportionation, that is, $CH_4 + CO_2$. Except for glycine and formamide, similar considerations hold for all N-organic compounds,²⁴⁾ that is, for most of biochemistry once again.

Since speciation and redox speciation will alter hydro- and lipophilities of many elements, biological resorption and subsequent transfers into media such as (mother's or animal) milk will also depend on pH and Eh potentials (Wünschmann, Fränzle and Markert, 2004; Wünschmann *et al.*, 2008). Of course, things are a little bit more complicated here: besides being locked up in either fat or mineral phases (bones, teeth), chemical elements must make it through various redox levels and membranes (guts, breast membrane) until eventually turning up in a medium which itself is heterogeneous, that is, an emulsion of fatty and aqueous liquid sub-phases, while certain elements might even then partition among these phases. For example, iodine exists in human milk in all various organoiodine compounds, iodide and iodate IO_3^- , the former distinctly lipophilic, the latter hydrophilic, while I^- will distribute among the phases. Likewise, sewage sludge contains appreciable lipid, and adsorption to limnetic sediments is favored by high $\log k_{ow}$. Actual transfer quotas into milk do not depend on either essential role or formal oxidation state so much but rather on the actual charge (due to both hydrolysis of aquaions and complexation). Hence, while Pourbaix diagrams give much more than some hint how to “modify” “embarrassing” chemical elements as to minimize both toxicity and bioavailability, biotechnological methods of

which behaves fairly similarly and which was isolated somewhat later in the nineteenth century accordingly was named after the daughter of Tantalos, Niobe eventually [originally, it was named columbium (symbol: Cb).

- 24) The formal potential (pH = 7) of glycine formation in oxidizing conditions according to:



is located above CO_2/CH_4 but below NO_3^-/N_2 (Shock, 1988). Thus, though glycine

most readily forms in prebiotic simulation experiments and gives rise to various more complicated organics when “energetized” itself, its thermodynamic equilibrium concentration will remain vanishingly small which is of obvious pertinence to prebiotic chemistry. For all other N-organics except formamide, these equilibrium levels are next to zero. Urea which is also fairly stable is no longer considered to be an organic compound now.

environmental engineering are concerned with yet more subtle partitioning effects. These effects can alter bioavailability of both metals and non-metals considerably.

In addition, corresponding effects influence the results of a safety analysis considerably but statements are limited to thermodynamically favored species as was mentioned before; that is, there is a tacit assumption that equilibrium is (almost) reached before the practical treatment process is terminated by the way it is run (note that, in a setup where the products are steadily removed from the system, actual equilibrium will never be reached!). Hence this is about the likelihood that kinetics can be brought close to equilibrium. In certain cases, kinetic influences can be deduced when knowing substituent patterns at inherently but modestly stable (i.e., aromatic) ring systems, controlling reactions in atmospheric, aquatic and biooxidative chemistry likewise (see below for details).

3.2.3

Reaction Kinetics and Hammett Equation

Hitherto in this volume environmentally relevant chemical reactions were considered tacitly assuming thermodynamic control but there are others, not or not completely proceeding to equilibrium as depicted by Pourbaix diagrams while the product to be considered misses from the diagram.

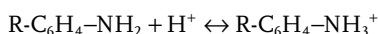
A reaction which affords such a product or even links an unstable educt speciation form to another likewise unstable one, which thus requires energy inputs cannot be forced to occur by adding a catalyst but takes energy input, for example, heating (shift of equilibria), light- or UV irradiation, electrochemical potentials or the like. Processes which entail release of free energy and formation of stable products, say reduction of N_2 to yield NH_4^+ , may occur spontaneously, or not, that is, being immeasurably slow unless there are appropriate catalysts. This is to explain that there is no general relationship between reaction kinetics and its thermodynamic aspects, with the problem rather more difficult in non-metal chemistry: activation barriers are lower in complexes. Even though chemical bonds are constructed by electrons, and direct withdrawal or addition of electrons by electrochemistry might be expected to overcome any such barrier, there actually still is considerable (and sometimes useful) selectivity which depends on the material of the electrode. The latter most often is not what it naively might be assumed to be: the only bulk metal which is not covered by an oxide or sulfide interface in aqueous or alcoholic media is gold. In all other cases, there are metal-semiconductor interfaces (Schottky diodes) embedded in the very electrode surface.

Yet it might be possible that relationships between kinetics and thermodynamics or substituent effects do exist for certain classes of compounds at least. As most of all compounds—including metal complexes are “organic” ones, it is likely that corresponding relationships would be seen with organics, and this is how it actually was.

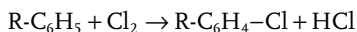
3.2.3.1 When Can Charge Density Patterns Control Kinetics of Entire (Larger) Molecules?

Chemical reactions are most likely to be influenced by substituent factors when in some—necessarily larger—molecule different kinds of functional groups do coexist. Certain possible reaction centres will respond to changes of charge density in remote sites also—when both are linked by systems of conjugated double or triple bonds—by altering reactivity in kinetic terms, whereas others will only “feel” local effects.²⁵⁾ Strangely, or at least remarkably, the former case—the entire molecule changing its properties (reaction kinetics) by some active substituents being located somewhere—is the one which can be described, tackled and eventually predicted much more readily:

larger (in molecular dimensions, of course), cyclic systems do respond more sensitively to replacing some H atoms at the ring something else exactly if charge density can be “distributed”. Delocalized cyclic electron systems are typical of so-called *aromatic compounds*. Their reaction kinetics are described by the *Hammett equation* which was derived about 1935 to describe such reactions during which aromatics exchange electrons with reaction partners (as a rule, give away electrons or electron pairs to the latter). Hammett-type kinetics are observed in both reversible reactions, such as hydrolysis or formation of benzoate esters (the classical system), protonations of aniline or pyridine color-change pH indicators, and additions of CO₂ or SO₃ (oleum, chlorosulfonic acid) to afford benzoic or benzenesulfonic acids, respectively, for example, according to:



and in irreversible transformations which, for example, entail production and release of hydrogen halides like in:



Corresponding “active” substituents R include R = -NO₂, -CN, -Cl, -OH, CH₃-CO-, -CH₃ or -COOH, each located in either the 3- (meta-) or 4-(para)- position to the substituent going to be newly linked or modified (ester, benzamide hydrolysis, etc.) at the benzenoid ring. We just alluded to the possibility that reactions which obey Hammett kinetics be reversible. Indeed the first investigations by L.P. Hammett (1894–1987) himself, starting in 1928, dealt with the protonation of organics like benzonitrils and nitrobenzenes in very strongly acidic media to determine the protonation capabilities of concentrated sulfuric and (a hazardous business) perchloric acids. Substituent effects of protonated or deprotonated groups differ considerably from those of the neutrals (Brown and Okamoto, 1958):

25) With hippuric acid (N-benzoyl glycine) or even some (1- or 2-) N-naphthoyl glycine, substituents located at the aromatic rings will influence reactions at benzoyl carbon (e.g., hydrolysis) or amino nitrogen (say, nitrosation) over long distances while the

same reactions will hardly depend by C₂ substitutions, that is, having benzoyl alanine or -valine although the substituents (methyl or isopropyl, respectively) are far closer.

benzene derivatives containing ammonium groups in anilinium salts are less reactive toward electrophiles than free anilines, benzoic acids or benzamides less so than benzoates. Besides kinetics of reactions in organic solvents such as acetic acid, acetone, methanol or CHCs to which it was originally (1930s–1970s) applied, the Hammett approach likewise works in water, other inorganic solvents like neat HF, HCN or H₂SO₄, NOCl, N₂O₄ (which themselves are nitrosating reagents), supercritical fluids and, actually, gases, mixed solvents or solids (e.g., the aromatic groups in lignite or lignin), including enzymes²⁶⁾ and crystals.

The Hammett equation already mentioned states an empirical (with the parameters also derived from measurement) relationship between the *logarithm* of reaction kinetics (to a first approximation, the activation barrier) taking place at an aromatic ring and the presence and influence of certain substituents at the ring. This is not just plain physical organic chemistry but most pertinent to environmental engineering as:

- 1) Aromatic compounds, including polycyclic ones (PAHs) are produced as pollutants/by-products during technical combustion processes.
- 2) They often pose ecotoxicological hazards, with some of these compounds—both unsubstituted ones like benzene, chrysene or benzo [a] pyrene and such ones additional functional groups like nitrobenzene or phorbol—being most potent carcinogenic or co-carcinogenic agents.

3.2.3.2 Chemical Properties of Aromatic Compounds

Benzenoid aromatics are pollutants—some of which provoke cancer—which are released during various chemical processes, above all combustion. There is a kind of “bulge” made of delocalized π -type electrons on either side of the aromatic ring which drives off species bearing free electron pairs themselves, for example, nucleophiles like ammonia NH₃ or cyanide CN⁻. Further, electron-deficient entities, all cations such as R-CO⁺, free halogens (Cl, Br, interhalogen compounds), other oxidants or “incomplete” metal complexes will readily react with this delocalized π -electron system to remove H⁺ or other groups. Thus both metal ions and protons (strong acids) are going to catalyze aromatic substitutions, for example, in the bromination by Br₂/FeBr₃.

If one knows or thus deduces kinetics for the principal reaction which produce or cleave some aromatic compound, one can estimate and predict whether certain aromatic compounds are going to pile up in the environment, perhaps so much as to exceed solubility and produce hardly attackable phases of their own (e.g., lumps of tar), or get degraded sufficiently fast not to reach substantial concentration levels of their own. Of course, an accumulation of secondaries is not at all

26) This refers to kinetics of aromatic substrate transformations catalyzed by enzymes (heme exoperoxidases, cytochrome P 450, indole oxidases) like oxidations of arenes, phenols, benzyl alcohols, aryl alkanes, alkyl-aryl sulfides or

indols including tryptophan to afford phenols, quinons or diphenols, benzaldehydes, sulfoxides and dyes (indigo, marine snail purple, melanine), respectively.

precluded by this, especially if the primary reaction at the aromatic ring translates into disactivation, like with aromatic nitrocompounds. Persistence of both benzenoid hydrocarbons and PAHs thus depends on:

- Abundances of suitable reaction partners like OH radicals,²⁷⁾
- The respective environmental compartment and, more so,
- Functional groups which already are or get bound to the aromatic ring(s).

Reactions at the very ring are irreversible,²⁸⁾ still allowing substituents once bound to an aromatic compound to be still modified chemicals but rarely cleaved again. This also holds for functional groups to be obtained from the atmosphere or from illuminated surface waters (OH, -NO₂, -O-NO₂). Generally speaking, electron-withdrawing groups cause electrophilic attack to slow down whereas electron-donor groups will enhance (speed up) kinetics. The quantitative extent of these effects is given by a so-called substituent parameter (see below), making the Hammett equation to read as follows:

$$\log k_1 = \log k_0 + \rho_j \cdot \sigma$$

k : rate constant;

ρ_j : reaction constant;

σ : substituent parameter.

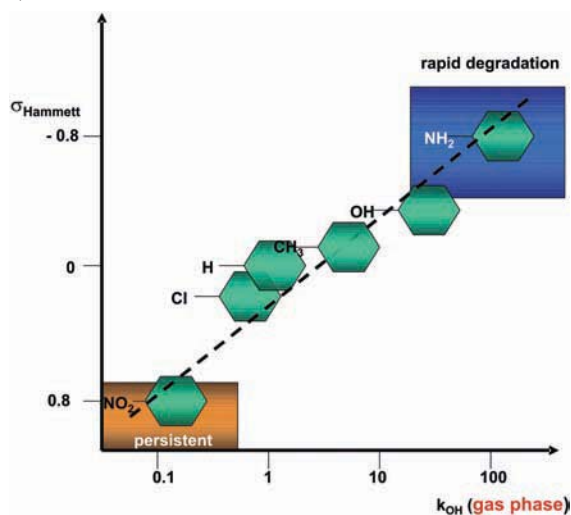
k_0 refers to the reaction rate without any substituent ($R = H$), that is to electrophilic substitutions which occur at simple benzene; σ_j is negative (<0). Accordingly, a positive substituent parameter like with nitro-, ester- or nitrile (-CN) groups will cause reaction kinetics toward electrophiles to slow down while a negative one spells faster kinetics. Thus some substituent displaying a parameter σ will change reaction speed from k_0 (for benzene) to k_1 ; the slope of the lines in Figure 3.9 generally depends on:

- 27) Remarkably, OH radical levels are virtually identical during daytime at sea level in intermediate latitudes in both troposphere and freshwater next to the surface unless the latter contains lots of carbonate or bromide ions:

One femtomol/l (aqueous solution) is tantamount to $6 \cdot 10^5$ OH-radicals/cm³ (air). An enhanced UV irradiation in mountain lakes, dissolved radionuclides ("radium wells"), dissolved hydrogen peroxide and/or certain metal ions and their photochemical transformations can considerably increase this value while in seawater it is going to be much smaller owing to higher levels of quenchers HCO₃⁻ and Br⁻. As levels are equal (in certain conditions), absolute reaction rates in troposphere and freshwater can be directly compared.

- 28) As noticed in the text, reversible reactions at aromatic rings include those with H⁺ [protonation of either ring heteroatoms (e.g., with pyridine) or of some substituent (amine, nitrile, carboxylate)], metal ions, that is, complex formation {both π - and σ -type, by addition of for example, [Os(NH₃)₃]²⁺ to a single formal double bond or of [Cr(CO)₃] to an entire ring as π -donors, or of pyridine, aniline, benzonitrile, phenyl isocyanide, or benzoate and so on ligands to a manifold of cation centers}, and sulfonation by or carboxylation by CO₂ [the latter takes place only with very electron-rich aromatics like phenyl anions (aryl metal compounds of Li, Mg, or Ca) or at phenolate ions].

a)



b)

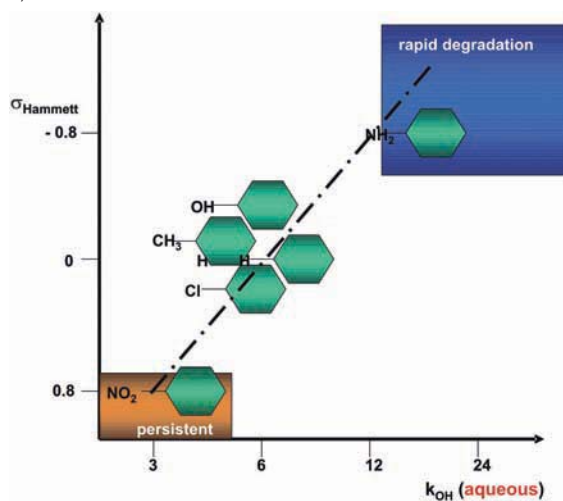


Figure 3.9 Some benzenoid aromatics actually occurring in polluted environments and their respective reaction rates in both air (a) and water (b) at 25 °C versus the Hammett coefficients of the substituents

(abscissa). Reactivities toward OH radical increase from persistent nitrobenzene to highly reactive aniline in either case but the size of difference depends on the medium of reaction.

- The reaction j which is investigated (here, attack by OH radicals);
- Solvent or medium [water, air, some non-aqueous solvent, soil liquid, solid humic matter, biomass (e.g., lipid)];
- Temperature.

Example: assume a reaction distinguished by $\rho_j = -3.0$ (a rather common value) which is going to be done at benzonitrile (phenyl cyanide) instead of benzene. For a cyano substituent in 4-position, σ_{CN} is about +0.66. This means $\rho_j \cdot \sigma_{\text{CN}} \approx -2.0$. Accordingly, the reaction is going to occur some 100 times slower (i.e., by $10^{-2.0}$ faster) at benzonitrile than at benzene.

As might be anticipated from the above considerations, describing the kinetics of both electrophilic²⁹⁾ and radical³⁰⁾ reactions at aromatic rings by some simple equation is the most precise and comprehensive at hand still now. While there are similar approaches to describe redox kinetics (the Marcus equation) and that of additions to alkenes (the Taft equation) but exactness of rate predictions is much poorer, and there is no comparable method for estimating kinetics of reactions at alkanes and other saturated compounds.

Slope and axis intercept of the line equation derived by Hammett are interpreted as a hint for mechanistic peculiarities of the reaction. Table 3.2 gives the (average) effect of several common substituents on reaction rate (logarithms) when the respective benzene derivatives react with either electrophilic agents or free radicals; σ values are taken from the classical paper by Brown and Okamoto (1958), with more recent work corroborating the high precision and validity of these values. σ values for radical substitution are taken from Kwok and Atkinson (1995) and are also used in a software package for estimating OH radical reaction rates toward aromatics in air.

σ values for both electrophilic and radical substitutions differ for the 3- and 4-positions in either case; hence σ_{meta} and σ_{para} values are separately listed. As a rule, second or, with compounds which are already substituted twice, third substitutions will take place either parallel in the 2- and 4-position or (else) selectively in the 3- (meta-)position, with but minute amounts of the other isomer formed, depending on the substituent already there (3- with nitro-, cyano- or ester groups). There is no Hammett correlation for product formation rates in the 2-position as there electronic reasons for faster or slower reaction are obscured by all steric hindrance (e.g., with branched alkyl groups in Friedel–Crafts alkylation) and

- 29) Even though free radicals like nitrogen oxides NO_2 and NO_3 or OH are both atypical and – notwithstanding their, for the latter two, extreme oxidant properties – also poor electrophiles, Hammett kinetics yet apply to their reactions with benzenoid or naphthenoid compounds also.
- 30) Substitution by radicals, like that by electrophiles, proceeds occur along an alternating sequence of addition- and elimination steps, namely:

- 1) $\bullet\text{OH}$ addition to the ring: $\text{C}_6\text{H}_6 + \bullet\text{OH} \rightarrow \bullet\text{C}_6\text{H}_6(\text{OH})$, then:
- 2) Reaction with dioxygen:
 $\bullet\text{C}_6\text{H}_6(\text{OH}) + \text{O}_2 \rightarrow \text{C}_6\text{H}_5(\text{OH}) + \bullet\text{HO}_2$, or:
- 3) In water [besides step (2)] oxidation by Fe(III) : $\bullet\text{C}_6\text{H}_6(\text{OH}) + \text{Fe(III)} \rightarrow \text{C}_6\text{H}_5(\text{OH}) + \text{Fe(II)} + \text{H}^+$

Table 3.2 Substituent parameters for both electrophilic and radical substitutions of benzenoid aromatics in the 3- and 4-positions.

Substituent	σ_{meta}	σ_{para}	$\sigma_{\text{meta}} (\text{radic.})$	$\sigma_{\text{para}} (\text{radic.})$
CH ₃	-0.069	-0.170	-0.066	-0.311
C ₆ H ₅ (phenyl)			0.109	-0.179
CHO			(0.36)	(0.22)
COOH		(0.4)	0.322	0.421
COOCH ₃	0.39	0.31	0.368	0.489
CO-CH ₃	0.376	0.502	(0.03)	(0.28)
CN	0.56	0.660	0.562	0.659
NH ₂			-0.16	-1.30
NH-phenyl			(-0.16)	-1.4
NO ₂	0.710	0.778	0.674	0.790
OH	0.121	-0.37	(0.121)	-0.92
OCH ₃	0.115	-0.268	0.047	-0.778
F	0.337	0.062	0.352	-0.073
Cl	0.373	0.227	0.399	-0.073
Br	0.391	0.232	0.405	0.150
I	0.352	0.18	0.359	0.135

Absolute reaction rates differ often among radicals versus (often cationic) electrophiles in solvents like water, because water is less prone for radical solvation. Accordingly, there are largest differences with hydrophilic primary substituents, most influencing water solubility of an aromatic substrate and the chances of electrophilic attack likewise, in the 4-positions of groups like OH, OCH₃, Cl. The ratio between the σ_{meta} - and σ_{para} -logarithms, that is, site selectivity, is a measure of site dirigation if divided by ρ_j (data taken from Hammett, 1973; Brown and Okamoto, 1958; Kwok and Atkinson, 1995).

intramolecular hydrogen bonds to link the already present (say, hydroxyl) and newly introduced groups. Differences among substituent parameters for 3- and 4-site substitutions are even more pronounced with radical reactions than with electrophilic ones for R = NH₂, OCH₃, Cl (columns 3 and 4 in Table 3.2). As a result, radical substitutions are even more regioselective.

Unless completely different reaction pathways are taken, for example, via excited-state intermediates or valence isomers like in photochemistry (which interconvert 3- and 4-isomers via benzvalenes, cf. photohydrolysis), aromatic compounds are *not* going to produce a bewildering mixture of secondaries. Kinetic statements will provide information which kinds of reaction cascades, introducing the same substituent taken from environment or purposely added as a reactant, one time after the other will bring about mineralization by secondary substitutions being faster³¹⁾ than with benzene or the like or rather the reaction will terminate

31) As activating substituents, that is, those distinguished by $\sigma < 0$, favor to replace the 2- and 4-positions, complete (hexakis-) substitution can be achieved, with the ring of the massively substituted molecule

going to break apart (while hexafluorobenzene, hexachlorobenzene or pentachlorophenol, -anisole may be readily prepared, there is no 1,2,3,4,5,6-hexaphenol, rather undergoing

sooner or later due to substituent effects. Of course, such predictions are feasible only if it is obvious from additional analytic information which reaction partners an aromatic molecule is going to encounter in an environmental compartment, for example, $\bullet\text{OH}$ or $\bullet\text{NO}_3$ radicals, hydroxylating enzymes or oxidantss such as chromate.

Radical substitutions by environmentally significant reactants like $\bullet\text{OH}$, $\bullet\text{NO}_2$ or $\bullet\text{NO}_3$ in the atmosphere, Hammett values rather similar to the “electrophilic” ones do apply. Strongly electron-withdrawing substituents like ester groups, however, will produce differences in the 4-position whereas $\sigma_{(\text{para}, \text{radic.})}$ is smaller than in ionic reactions of acetophenone (aromatic methyl ketones, including musk fragrances), fluoro-, chloro-, or bromobenzenes, phenols and anisols. ρ_j is known to be negative. When free radicals like OH are available in larger amounts, anisols, ethoxybenzenes, or halobenzenes are more readily converted into corresponding phenols (alkoxy-, halophenols) and other radical addition and secondary condensation products than simple benzenoid aromatics, with benzoate esters displaying still lower reactivity. This refers to many herbicides (aryl carbamates) as well as to sunblockers which get into environment also during lake swimming and the like. If the substitution (hydroxylation) products are less prone to microbial³²⁾ degradation, they might pose toxicological problems.

In certain cases, there may be yet other reaction pathways which are even more favored. Diphenyl amines like the analgetic agent diclofenac should be most reactive toward free radicals with $\sigma_{(\text{para}, \text{radic.})} = -1.4$, but in aquatic media photoisomerization to yield the corresponding carbazol (dibenzopyrrol) is faster than OH attack even though the acetate group and the two chlorosubstituents should further enhance OH reactivity (close to diffusion limit). The produced trisubstituted [dichloroacetato- or (after decarboxylation) dichloromethyl] carbazol is rather persistent and will enrich in surface waters like Lake Greifensee near Zurich (Switzerland) where it was first detected (Poiger, Buser, and Müller, 2001). The Hammett equation does not cover such processes. With metal complexes and semiconductor sorbents like Bi_2O_3 added to the suspension, diclofenac is even

cycloreversion and tautomerization into glyoxal if preparation is tried).

Disactivating (i.e., $\sigma > 0$) substituents like nitrogroups form 3-substituted products which are not eager to react any further (toluene can be easily nitrated, nitrotoluene takes more vigorous conditions to do so, and preparation of TNT explosive eventually is accomplished by some sideway escaping the joint disactivation by two nitro groups). Although nitration is thus self-terminating, polynitroarenes from ammunition production may be reactivated by partial reduction into—themselves highly toxic—nitroanilines by all soil bacteria, reactive walls or certain solid sulfides, going to be further processed in

either in a biochemical or oxidative pathway.

Fungi, especially wood-decomposing basidiomycetes, can produce free radicals including OH by means of—mostly Mn-containing—exoperoxidases (Williams and Frausto daSilva, 1996) which can attack stable polymeric, partly aromatic organic compounds like lignin (but leave behind cellulose) and even lignite. Thus, corresponding enzymes achieve a specific degradation of functionalized aromatic materials. With $\sigma_{(\text{para}, \text{radic.})}$ and the analogous parameter $\sigma_{(\text{meta}, \text{radic.})}$ for OH substituents being strongly negative at -0.91 , the reaction will proceed even swifter into mineralization.

32)

Table 3.3 Reactivity modifications in naphthalenes. Here, $\sigma_{\text{para (radic.)}}$ denotes the logarithm of relative reaction rate of an aromatic (here: naphthene) compound para to radicals at benzene, divided by ρ_j ; $k_{\text{OH (air)}}$: reaction constant; $\log k_{\text{rel.}}$. Logarithm of reaction rate in the substituted naphthalene versus naphthalene itself.

Compound	$\sigma_{\text{para (radic.)}}$	$k_{\text{OH (air)}}$	$\log k_{\text{rel.}}$
Naphthalene	0	21.6	0
1-Methylnaphthalene	-0.311	53.0	0.39
2-Methylnaphthalene	-0.311	52.3	0.39
1-Naphthol	-0.92	ca. 550 (!)	1.4
1-Nitronaphthalene	+0.790	5.4	-0.60
2-Nitronaphthalene	+0.790	5.6	-0.59

more readily degraded than diphenylamine while carbazol does not undergo this kind of sensitized photooxidation. Hydroxylation product intermediates could not be isolated but there is some fragment transfer toward glycinate ion (Fränze *et al.*, 2010).

In a manner analogous to Table 3.2 empirical reaction rates (Table 3.3) for reactions between some naphthalenes and OH radicals were used to determine $\rho_{j(\text{radic.})}$ for a system relevant in environmental chemistry. Naphthalenes are double-ring annelated (unlike biphenyls, fluorenes, benzofuranes) aromatic compounds which behave much like benzenoid aromatics also toward OH, with reaction rates considerably increasing from nitronaphthalenes over the simple compound and methylnaphthalenes (two isomers) to naphthols, being generally much higher than in nitrobenzene to phenol. There is one single substituent altering charge density above and below two rings rather than one now, reducing effects of substitution somewhat, with naphthol being some 100 times more reactive than nitronaphthalenes while the corresponding factor between phenol and nitrobenzene is about 180. We do this explicitly to get an estimate for reaction rates of isomeric chloronaphthalenes large amounts of which were detected in polluted ground waters below the city of Bitterfeld (Saxony-Anhalt, Germany; Kopinke *et al.*, 2000).

The isomer does not matter between methylnaphthalenes, with the difference in reaction rates given being smaller than the experimental error in measuring these rates while ρ_j is -1.08. Accordingly, for chloronaphthalenes ($\sigma_{\text{para[Cl]}} = +0.227$) $k_{\text{OH}} \approx k_{\text{OH [naphthalene]}} \cdot 10^{-0.227 \cdot 1.08} = 10^{-0.245} \cdot 21.6 = 12.2$.³³⁾

As suggested before, if some (benzenoid-aromatic or PAH) chemical in the environment is subjected to several chemical reactions one by one, both novel substituents will bind to the ring(s) and those already there might be modified

33) With 1,4-dichloronaphthalene there is another halving of the rate constant toward OH radicals down to a measured 5.8.

(oxidations of methyl-, amino-, or $-\text{CH}_2\text{OH}$ groups). Both this and increased hydrophilicity and decreased vapor pressures caused by such transformations will alter $\log k_{\text{ow}}$ and the tendency of secondary, tertiary . . . reactions to occur in aqueous rather than air phase. We noticed before that this does matter concerning the reaction rates and thus persistence of primary and secondary products, with slopes of line equations getting altered. While consecutive hydroxylation will cause the ring(s) to take up OH ever more rapidly until they break down (mineralization), multiple nitration (which, e.g., occurs photoassisted in rain-water) will produce persistent pollutants (cf. Figure 3.9). Although reactivities obey to the same rules in air and aqueous media, the relative ranges of reactivities are quite different (factor 800 vs factor 4.4) which causes the reaction products to be unevenly distributed across the parameter field of persistence (Figure 3.10). To give a practical example, one can guess using these data what will happen to some benzenoid hydrocarbon (toluene, xylene solvents, alkyl phenol tensides, aryl carbamate insecticide) in partitioning between air and water if: (i) there is a high level of higher nitrogen oxides in the atmosphere (polluted, night-time) or (ii) much OH in water [Fe(III), ozone + organics; daytime, intense UV], causing either lots of nitroaromatics or lots of phenols, quinones to form first.

3.2.3.3 Kinetic Modeling of Reactions at Non-aromatic Unsaturated Hydrocarbons by the Taft Equation

There is a description for reaction kinetics which formally resembles that for benzenoid and naphthenoid aromatics. The Taft equation covers additions to or cleavages of alkenes (olefins, e.g., ozonolysis, reactions with periodate or permanganate), also applies to alkynes to some extent, reading:

$$I = \rho_I \cdot \sigma_I$$

Here, σ_I denotes an inductive effect (extent of charge transfer toward next C center) caused by some substituent. Here, like in the Hammett approach, we deal with both reversible (protolysis, the prototypical reaction being effects on acidity of substituted acetic acids $\text{X}-\text{CH}_2-\text{COOH}$) and irreversible, such as epoxidation³⁴⁾ or formation of glycol diesters (oxidations by chromate and its derivatives like CrO_3Cl^- , by MnO_4^- or OsO_4 or OsO_3N^- ; Sharpless, 2002) by oxidant attacks. ρ_I once again is a scaling constant, for example, 0.262 (Hammett, 1973) for room temperature acidities of acetic acids. Even though this and many other reactions or their substituent effects can be described by the Taft approach reasonably accurately, it fails with respect to radical reactions, like H transfer by OH radicals at methane derivatives CH_3X [$\text{X} = \text{H}, \text{CH}_3$ (including weighting factors), F, Cl, Br, I, CN, $-\text{NO}_2$, $-\text{CCl}_3$, etc.]. The same holds for other oxidants, be it oxometallates or ozone, or

34) Epoxidation does not extend to alkynes as oxirenes are no minima on the potential hypersurface; rather, ketenes are formed directly by simultaneous H or R (alkyl,

aryl) shift to the next C atom. In aqueous media, (branched) carboxylates are going to be isolated by instantaneous ketene hydrolysis.

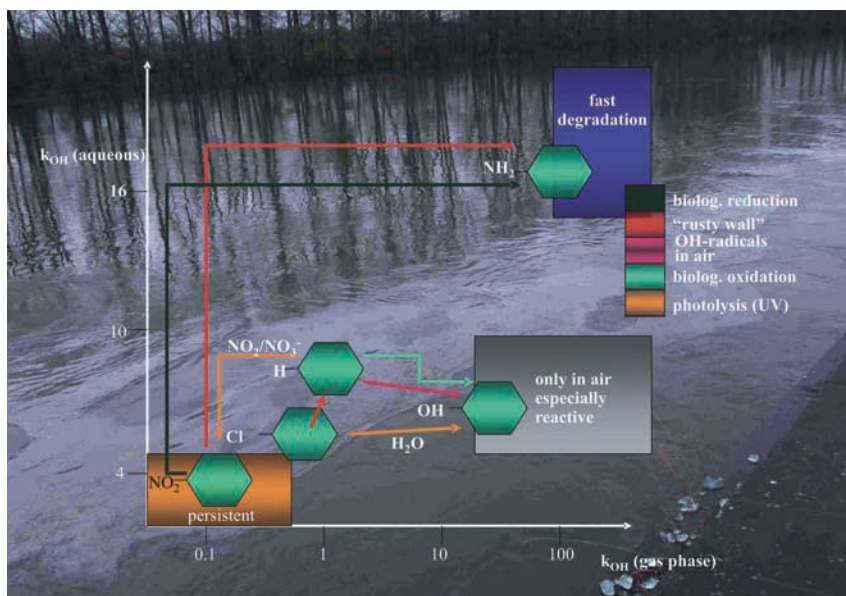


Figure 3.10 Five simple prototypical benzenoid compounds (benzene, chloro- and nitrobenzene, phenol and aniline) are subjected to various reagents coded by different colors or to biochemical transformations. Reactivity increases diagonally through the diagram from left bottom to top right, less so in water than in air. Reductions—both by soil bacteria and the action of reactive walls made from iron toward chloro- or nitrobenzene—will increase residue reactivities, as does photochemical arene hydrolysis of chlorobenzene, which affords phenol. In stark contrast, aqueous photoreactions in media which contain dissolved NO_2 or nitrate makes nitrobenzene from benzene, reducing reactivity and increasing persistence (arrow to lower left side of diagram). The same holds for nitrated alkylbenzenes (nitrotoluenes) or phenols, after exposition of alkylbenzenes, phenols, cresols to NO_2 -dependent photooxidation. Air polluted by NO_2 or eutrophicated, nitrate-rich water hence both will bring about

formation of products which are not only much more persistent than the “original” benzenoid or biphenyl or PAH aromatics but also more toxic to all plants, vertebrates and many other organisms. This will happen even when $\text{NO}_x^{(-)}$ -based pathways outcompete attack by OH. The orange color of the corresponding area in product physico-chemical properties is meant to be understood as a kind of alert signal while bright blue (like clean air, water) is to symbolize rapid degradation of the above hazardous substances. The arrows provide a network from which it can be deduced what will happen if several transformations occur one after the other. Certain of these transformation will occur or are even designed to be run in soil, rather than air or water, also, of course except of photochemical reactions. Photograph by courtesy of: www.ff-nienburg.de; scheme overlaid by the authors.

oxidations of alcohols and their esters, halides XCH_2Y [for X see above, $\text{Y} = \text{Hal}$, $\text{OC(O)R}'$, $\text{OSO}_3\text{R}'$] by dimethyl sulfoxide (DMSO) to afford aldehydes or ketones. This is partly due to the Taft equation, unlike the Hammett equation, explicitly referring to equilibrium constants (by definition of reversible reactions only) rather than kinetics whatsoever.

This is to say that predictions of environmentally pertinent reactions—concerning kinetics of organic transformations and thus of the possible spreading of respective compounds/ions by air or water drift across the environment—by means of correlations familiar from physical organic chemistry are essentially limited to aromatics whereas there is some reliability for estimates on alkene and alkyne cleavages and there are similar incremental (rather than producing equations like those above) approaches for OH and NO₃ attacks on certain functional (alkyl, haloalkyl) groups of alkanes also (Kwok and Atkinson, 1995).

In addition, the (reaction kinetic) behavior of very small saturated molecules can be determined by calculating the potential hypersurface linking the reaction partners directly, by calculating shape and width and height of the activation barrier by means of *ab initio* quantum chemistry. Except for this, correlations with redox potentials of reaction partners do best.³⁵⁾ There is a deep-rooted theory for electron-transfer kinetics in pairs of reactants (Marcus theory; R.A. Marcus, Nobel prize for chemistry 1992) which however contains so many parameters which can or must be empirically adjusted that comparisons or actual predictions are possible only as long as one of the partners is kept very similar. Accordingly, there are few pertinent investigations within environmental chemistry, for example, on oxidations of aqueous phenols by singlet oxygen ¹O₂ (Mártire and Gonzalez, 2000), with phenols including cresols, halogenated phenols and tyrosine.

3.2.3.4 Partition of Volatile Aromatics and Their Respective Oxidation Kinetics between Air and Water: Practical Examples from Environmental Chemistry

In the environment, benzene will react with all OH radicals, ozone and certain nitrogen oxides, and in addition it is going to be consumed by microbes. In both the first and last cases, hydroxylation prevails to first produce phenol. From the Hammett equation one can obtain the drawbacks for secondary transformation kinetics in either air or water. The slope and intercept of reaction kinetics depend on temperature, solvent (which is absent in gaseous phases) etc. Here *T* is 25 °C, water is a fairly poor (weakly shielding) solvent, yet substituents like OH, OCH₃ or NH₂ bring about much more of an increase in reactivity toward OH radical in air than in water. These substituents cause hydrogen bonding toward water and hence more shielding by H₂O solvation than in benzene or alkylbenzenes (the OH radical has to make its way through a solvent cage, unlike in air), thus the rates of hydroxylation are less increased versus benzene than in air. Conversely, lifetimes (about two weeks for benzene, chlorobenzene in air) will be less reduced than would happen in the gas phase. If the compound is or becomes less volatile and more hydrophilic with substitution, this relative reduction of reactivity will allow the product to accumulate in water (and, with PAHs, which are sufficiently

35) The first author (S.F.) did corresponding work while with UFZ Environmental Research Center, working out correlation between OH (or NO₃) reaction kinetics (log *k*_{in}, like with Hammett correlations) and the 1-e oxidation half-wave potentials of

PAHs, amides, anilines, and many groups of other organic compounds. The regression lines referred to one kind of organic compounds only in each case (Fränzle and Schüürmann, 2000).

lipophilic, to undergo biomagnification). Figure 3.10 gives a selection from transitions of benzenoid aromatics to be expected in the environment and their effects on forthcoming reactions. If the newly introduced functional groups, like OH, increase reactivity in the environmental compartment in which the pollutant happens to be, the secondary, tertiary . . . steps will speed up, with the ring system breaking apart sooner or later. Nitrations on the other hand slow down secondary reactions so much that the primaries will pile up unless for other reactions becoming possible in aqueous media.

But this is only some part of the story: besides of changes in reactivities in biomass, air or water by first substitutions like hydroxylation, volatilities will also change, as will the Henry constants. As partition among air and water does directly influence lifetimes of organics, and organic reduction products, while still hydrophilic and far less volatile than benzene (aniline from nitrobenzene), can react again fast even though aniline OH reactivity in H_2O is about nine times that of nitrobenzene (as opposed to a factor of some 850 in air), effects of volatility and solubility will become superposed. The results are given for the seven compounds discussed in Table 3.4.

If chlorobenzene is reduced to yield benzene, reactivities will not alter significantly in either air or water but volatility does increase some eight times. Hence, secondary reactions at benzene will be shifted into the aerial phase with respect to chlorobenzene. When benzene gets hydroxylated to produce phenol, the vapor pressure is reduced by some factor of 230 while water solubility is increased about 100 times. Subsequent processes accordingly are expected to occur in water rather than air. Nitrobenzene reduction into aniline will not change vapor pressure too much. The last two columns of Table 3.4 reveal how reaction shares of aromatic compounds will be distributed between air and water assuming sufficiently many OH radicals will be available in either medium on the long run also (recall that levels are almost identical in the troposphere and freshwater in moderate climates near sea level!).

Unlike the reference compound benzene, all aniline, benzonitrile, nitrobenzene and phenol will be processed in water almost exclusively, mostly so for chlorobenzene also while methylation means that toluene will keep on reacting in air more than benzene does. Changes of solubility and reactivity by hydroxylating benzenoid hydrocarbons apply to substituted benzenes as well: water solubilities of phenols are 15–20 times better (for the basic compound, even 100 times), while vapor pressures are about a 100 times smaller. Accordingly hydroxylation causes subsequent reactions to occur in water rather than air. When BTEX aromatics (benzene, toluene, ethyl benzene, xylenes) are vented into air from fuels or solvents (toluene being a popular solvent in glue preparations), the final result will be *water* pollution which raises more concerns since phenols are most toxic to limnetic animals.

Sometimes it takes a secondary (re-)activation by an intermediate reduction step—be it achieved by catalytic hydrogenation or electrochemistry—to make efficient degradation by soli organisms possible at all, for example, with certain halogenated aromatics or multiply nitrated residues from producing explosives or

Table 3.4 Parameters and reaction rates toward OH radicals which are relevant for the distributions of seven typical benzenoid aromatics if saturated in both air and water.

Compound	Vapor pressure at 25 °C (kPa)	Boiling point (°C)	Water solubility in mg (mmol)/l	k_{OH} (air)	k_{OH} (water)	Reaction rate ^{a)} in air (–; relative to benzene = 1)	Reaction rate in water (–; relative to benzene = 1)
Benzene	12.7	80.1	800 (10.2)	1.23	7.8	15.6 (1.00)	80 (1.00)
Nitrobenzene	0.030	210.7	1900 (15.4)	0.15	3.2	0.0045 (2.9×10^{-4})	49 (0.61)
Benzonitrile (cyanobenzene)	0.110	191.1	10000 (97)	0.33	5	0.036 (2.3×10^{-3})	485 (6.1)
Chlorobenzene	1.60	131.7	300 (2.7)	0.77	4.5	1.23 (0.08)	12 (0.15)
Toluene	3.79	110.6	500 (5.5)	5.96	3.0	22.6 (1.45)	16.5 (0.21)
Phenol	0.055	181.8	86000 (915)	26.3	16	1.45 (0.09)	13.000 (163)
Aniline	0.090	184.2	40000 (430)	111	17	10.0 (0.64)	7300 (91)

a) Reaction rate is the substance turnover per volume of the corresponding environmental compartment here. This relative reaction rate will result once partition equilibrium was established between air and water phases given the corresponding data for vapor pressure and water solubility.

polymers.³⁶⁾ If nitrobenzene is reduced to afford aniline, for example, by solid sulfides or some soil bacteria (which, however, cannot process multiply nitrated benzenes or naphthalenes [formed in rainwater (Maddigapu *et al.*, 2011)] into nitroanilines or naphthylamines the products are still so poorly volatile that subsequent reactions will also proceed in water or ground water rather than air, while reaction rates are considerably higher than in unchanged polynitroaromatics due to the different (sum of) Hammett parameters.

Both biotic and abiotic transformations thus cause “shifts” among the environmental compartments in a way which can be systematically predicted. Concerning biomass it should be mentioned that biological accumulation of benzenoid organics can likewise be described using correlation between ρ_{Hammett} and $\log k_{\text{OW}}$ (Fränzle, 1993). For stabilities of metal complexes, the equation by Fränzle (2010) to describe and predict corresponding formation constants, is likewise related to ρ_{Hammett} . There is a relationship between ρ_{Hammett} and the electrochemical ligand parameter (Fielder *et al.*, 1995) of complex ligands, implying an indirect relationship between ρ_{Hammett} of a functional group corresponding to the (oxidized form of) ligand (e.g., NO_2 rather than NO_2^-) and complex stability which also holds for substituent effects in arylated ligands (aryl phosphanes, benzonitriles, pyridines, etc.).

3.2.4

Activation Barriers versus Catalysis

Not all exothermic chemical reactions do proceed at an appreciable rate at room temperature. Otherwise, we would not be here since Earth's atmosphere contains substantial (about 21%) oxygen and biogenic organic matter other than wood or straw can also be combusted (oxidized while releasing large amounts of energy) by contact with O_2 . In terms of environmental engineering this means that substances which could readily and completely degrade in air will yet persist or are difficult to remove. What are the reasons of this relative chemical inertness and how it might be overcome?

3.2.4.1 Reaction Kinetics and Mutual Repulsion among Molecules

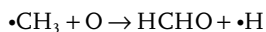
When considering Hammett kinetics we were already concerned with the fact that “aromatic” organics would not or hardly undergo certain kinds of reactions (i.e., nucleophilic substitution) since the electron system along the ring and the electron pairs of nucleophiles mutually repel each other while electrophilic agents do readily attack, an obvious outgrowth of the fact that like electric charges cause

36) Catalytic hydrogenation takes place at nickel or noble-metal interfaces, with dihydrogen (electrochemically produced from water at the very interface) or formic acid or alcohols/sugars used as H sources. Residues from TNT production during World War II are still present at high levels, essentially unchanged, for example,

around former ammunition production site Werk Tanne in Saxony-Anhalt (Germany) almost 70 years after. Dinitrotoluenes which also are explosives although less vigorous than TNT are reduced and carbonylated to make aryl bis-isocyanates for polyurethane polymer manufacturing.

repulsion while unlike (positive and negative) will mutually attract. Recall that the outer parts of any chemical species (including the proton which will not go along un-coordinated in any kind of condensed matter) consists of electrons which form a layer of negative charge faced toward like layers of negative charge.

Hence there usually is an activation barrier for reaction among molecules or radicals [but not between: (i) cations and (ii) atoms, radicals or molecules], with a notable exception relevant for both cosmochemistry and combustion in engines, namely formation of formaldehyde HCHO which is rather common in interstellar gas and gets locked up into comets. It is produced by reaction of methyl radicals with O atoms even at cryogenic temperatures [E_{act} and thus thermokinetic rate effect being next to zero from 100 K to white heat (internal combustion engines)]:



This reaction which does quite readily occur (close to diffusion control) gets its environmental effect from attempts exactly to make internal combustion in motors better controlled and more benign to environment: anti-knock agents in fuel, nowadays ethers like methyl tert-butyl ether (MTBE), besides organomanganese reagent $\text{CpMn}(\text{CH}_3)(\text{CO})_2$ (cymantren), acetone or ethanol which did luckily phase out lead tetra alkyls, all serve to produce methyl or ethyl radicals. Besides, oxygen atoms also arise during initial steps of combustion. Then O and CH_3 react like above, at a rate which does not depend on temperature, and hence take over when the expanding gas above the piston is rapidly cooled down. The final result is freeze-out of HCHO and other aldehydes which thus make their way into the exhaust gases. By the way, O atoms and methyl radicals (co-)adsorbed at an appropriate³⁷⁾ interface will react in the same manner, forming HCHO there. This also happens on platinum (with O_{ads} from N oxides); thus a three-way catalytic converter does produce aldehydes, mainly HCHO itself, when still attending its working temperature. This can be demonstrated by using Dräger tubes [sensitive to aldehydes, benzene, crude oil hydrocarbons (e.g., hexane) and nitrogen oxides, respectively] for regularly sampling the exhaust gas mixture of an Otto four-stroke engine after cold start about once per minute. Aldehydes are lachrymatory irritants, some of them carcinogenic, and form important components of summertime smog.

Except from such cases, just a minute fraction of encounters (hits) between the reactants—hits which provide: (i) the proper orientation of reaction partners in space and (ii) the relatively highest kinetic energy—brings about a reaction. The formal description is given by the Arrhenius equation where:

$$k = A * e^{-(\Delta G^\ddagger / RT)}$$

k = rate constant,

A = frequency of hits among the reaction partners,

37) An appropriate interface is one which does not favor homogeneous coupling to produce ethane and O_2 , respectively nor is it, like lead, bismuth or antimony, consumed by methyl radicals to produce

volatile element polymethyls (Paneth's metal mirror test for CH_3 radicals; Friedrich Adolf Paneth, German Austrian chemist, 1887–1958).

$\Delta G^\ddagger$ = activation energy (barrier height),

R = kinetic gas constant (per mole, which is the average thermal energy of 1 mol of gas at 1 K,³⁸⁾ namely $8.314 \text{ J}/(\text{Mol}\cdot\text{K})$.

If the activation barrier is sufficiently high, no reaction (detectable turnover) will occur within usual experimental timescales at room temperature or even at red heat, for example, there is no hydrogenation of N_2 although the reaction is exothermic. Typical values for activation barriers are $\Delta G^\ddagger = 50\text{--}100 \text{ kJ/mol}$, as compared to room temperature $\approx 2.5 \text{ kJ/mol}$ at ambient temperature. Hence, just one among $\geq e^{20} \approx 4 \cdot 10^8$ collisions among molecules will cause a reaction. The collision rate at ambient temperature and pressure is of order $10^{10}/\text{s}$, with just a small fraction of these hits providing a reactive orientation among the molecules. This means that gas phase reactions distinguished by $\Delta G^\ddagger = 50 \text{ kJ/mol}$ will take place within some seconds at room temperature, 1 bar, while those with just double as high an activation barrier ($\Delta G^\ddagger = 100 \text{ kJ/mol}$) will take about a billion times longer, that is, about 100 years.

3.2.4.2 Kinetics, Catalysis, Equilibrium

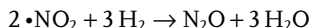
If $\Delta G^\ddagger$ is so large as to provide unacceptably slow (impractical) kinetics of some chemical reaction, the activation barrier may be reduced in size by applying some *catalyst* (or by producing excited states of one or more reactants, mostly by photochemical means; see also Section 3.2.2).

A substance, which is dubbed the catalyst, is added to the reaction mixture and interferes with the reaction without being used up or transformed permanently. Staying behind, it can (theoretically) speed up the reaction forever or as long as new reactants are admitted. For example, a mixture of hydrogen and oxygen is perfectly stable at room temperature also within the ignition limits (some 4 and 96% H_2 , respectively); there will be no explosion. If, however, some platinum sponge is brought into the gas mixture, it will explode immediately. Here, the effect of catalysis is a dramatic decrease of ignition temperature whereas in other cases the result will be “just” an enhancement of reaction speed (often, that of but one pathway of several possible ones, increasing selectivity of transformation). That is what a catalyst can do, but it would not, never, alter the state of chemical equilibrium. After passing once through the catalytic cycle the reaction are removed from the catalyst (interface, molecule or complex) once again—otherwise it would not remain available for binding and reacting new substrate species.

Most somewhat bigger molecules but also many atomic ions and small-molecule pollutants like NO_2 can undergo lots of different reactions, both if ambient conditions are varied and if there is a constant set of reaction partners. Then a single pollutant will give rise to a complicated mixture of secondary chemical species which cannot all be expected to be harmless. For example, nitrogen oxides react with H_2 or hydrocarbons not only to yield dinitrogen (the “optimal” product) but can afford N_2O , NH_3 and organonitrogens such as oximes and nitriles as well;

38) The only chemical species still to display any noticeable vapor pressure at 1 K is elemental helium.

ammonia and nitriles are toxic, while N_2O is a long-lived greenhouse gas. Each of these various reaction pathways like:



has an activation barrier of its own which determines its reaction rate while a corresponding catalyst will retain the products at the interface or metal atom center differently well, perhaps up to catalyst poisoning. Hence they are going to be desorbed and replaced by novel substrate at different rates which controls the distribution of products, with the catalytic cycle often determined in kinetics by product cleavage. This will hold the more the more reactive corresponding products are³⁹⁾ but CO_2 will not be easily removed from any kind of interface either.

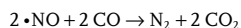
By proper choice of all catalyst, reaction temperature and possibly additions to the catalysts reactions of, for example, NO_2 can be made product-selective, going into a certain direction with a single reaction pathway and product to dominate. Platinum–rhodium alloys⁴⁰⁾ will convert both mixtures of N oxides and ammonia selectively into NO, which then continues to react with CO to give N_2 and CO_2 once it meets another contact⁴¹⁾ in the heterogeneous configured three-way catalytic converter. Selective transformations of other compounds in technical chemistry is achieved along the same way of reasoning: one telling example is ammonoxidation, the coupled oxidation of 1-alkenes and NH_3 to afford nitriles which occurs at Mo-doped⁴²⁾ Bi_2O_3 at some 400 °C. Likewise, enzymes bring about high selectivity by just weak binding of products, supported by sterical effects (“molecular recognition”). This selectivity, attacking one or few sides in a biomolecule which might actually react at hundreds of sites if it is a polymer like a protein,

39) This is not a contradiction with catalysts promoting exothermic reactions only: there are highly exothermic reactions the products of which are rather reactive, for example, corroding, in other ways, say the reaction between hydrogen and chlorine which affords HCl. Similarly CH_4 reactions with nitrogen oxides can be followed by metal dissolution once HCN is produced.

40) The same alloys are now being used for producing nitric acid by oxidizing ammonia for almost a century (“Ostwald catalyst” for “ammonia combustion”). Selectivity into NO product on a Pt/Rh alloy, starting with either NH_3 in ammonia combustion or NO_2 in three-way catalytic exhaust converters is caused by its being but loosely adsorbed on this alloy, unlike on copper or ruthenium. NO thus leaves the surface to undergo other reactions elsewhere, while on Ru, where it is almost irreversibly adsorbed (also cf. the stability of Ru nitrosyl complexes!) and thus open to further reductions by CO, hydrogen or hydrocarbons to eventually yield ammonia.

Hence one should not use ruthenium in a three-way converter even though it is unique in activating hydrocarbons which either escaped combustion or were formed *de novo*.

41) The strongly exothermic reaction:



will occur at most diverse surfaces, including charcoal, at several hundred °C. This is the principal energizing step in gunpowder reactions, allowing it to either explode or propel rockets (NO here is formed from K nitrate, CO from incomplete combustion of coal itself).

42) In solid-state chemistry and microelectronics, “doping” a material (most often, a semiconductor like Si or GaAs) just refers to doing some chemical addition to alter (improve) its performance. Given this, this notion of “doping” is actually quite related to that of pharmaceutical (ab)use in sports: the properties of an athlete’s body are also altered by chemical addition . . .

makes a meaningful transformation out of a muddle of rather random reactions. Enzymes, being biological/biochemical catalysts, usually interact with one well-defined site in the substrate (not necessarily the one which would be most reactive) to promote just one of the imaginable reactions of this substrate.

So enzymes also have their role in environmental engineering even though there are many cases where complete rather than partial or selective transformations are wanted: in fuel cells, C-containing fuels like methanol or hydrocarbons (gasoline) should be degraded (oxidized) all the way into CO_2 , and the same holds for hydrocarbon removal in cleaning soils or other environmental sites. While in the latter case some microbes (and their oxidation enzymes) will perform pretty well (Lovley *et al.*, 1987), CH activation in alkanes is so demanding (Rothenberg, 2008) that ruthenium (world annual production some 30 t only) is the element of choice still.⁴³⁾

Even though a catalyst will get out of the transformation virtually unchanged, it can only interfere with the reaction and enhance its rate if there is at least some surface reactivity taken to bind, disassemble and rearrange (adsorbed fragments of) molecules: those platinum group metals palladium and platinum or ruthenium which are attacked by *aqua regia* or even (Pd) nitric acid, also display much more diverse heterogeneous catalysis than the less reactive osmium⁴⁴⁾ and iridium (neither of which dissolves in *aqua regia* which marked the start of their isolation and identification by Tennant in 1804). The same holds for gold which is the only metal which would not cover by at least a few atom layers of oxide if exposed to air. We shall look on these uppermost layers soon.

3.2.4.3 Homogeneous versus Heterogeneous Catalysis

There can be two different kinds in which the catalyst can get into contact with its substrates:

- It may be dispersed in it, even dissolved as a complex ion or miscible liquid (gases are generally miscible among each other).
- It may form a separate, solid or liquid which stays aside, interacting only across some common interface which separates the two phases⁴⁵⁾ and it is there where the action is.

43) Alkane or arylalkane CH activation or CC cleavage by metal complexes rarely succeeds unless photoactivated or -assisted and even then requires platinum group metal (PGM) centers (Rh, Ir, or Ru again); so it offers no real alternative. Methanol oxidation into CO (ligands) or HCO_3^- can be achieved by quite a number of metal complexes, but once again those containing platinum group metals definitely prevail. There is still much to do for biomimetic catalytic chemistry.

44) This is why, opposed to consumption of some 200 t/year in Pd and Pt and several

dozen t/year in Ru or Rh, there is virtually no chemical use for osmium now other than volatile OsO_4 oxidant sometimes still being used for histological staining even though a $\text{OsO}_2/\text{TiO}_2$ mixture was the first identified effective catalyst for N_2 hydrogenation into ammonia back in 1909. Global osmium production now is <200 kg/year (which would make up a cube of less than 20 cm size!).

45) This is why heterogeneous catalysts are often called "contacts" in technical organic chemistry.

Three effects can be distinguished which (may) contribute to a sorbent acting as a catalyst:

- 1) Adsorption increases concentration of a gaseous or dissolved substance at an interface from a few mmol/l up to 30 mol/l in layers which are several atomic layers thick. Hence one can expect reaction rates to increase vastly because molecules now hit each other much more often within the adlayer; however, they are no longer freely mobile along the three axes, and reactive collisions are partly precluded by certain orientations in space close to the sorbing interface. Further, sorption will likely polarize some potential reaction partner also within a molecule, rendering it more active toward either nucleophiles or oxidants. This is related to the second activating effect, namely:
 - 2) The sorbent (to act as a heterogeneous catalyst) will withdraw charge density from the adsorbed molecules, thus reducing mutual repulsion among electron hulls of these molecules. As a rule, aromatic compounds do not undergo additions of H_2 , hydrogen halides or water to produce (halogenated) cyclohexanes or cyclohexanetrioles, they do adsorb onto all Pt, Ru or Ni with the rings lying "flat" on the metal surface to which most of the charge of π electrons gets donated. If two materials are contacted to each other, that one with higher dielectric constant or lower electron work function (EWF) will attend a positive charge with the other taking up electrons (Volta's contact potential). Accordingly the most heavy 5d metals Re through Au with EWFs > 5.5 eV and p-type semiconductors (among which for example, NiO and Bi_2O_3 are potent heterogeneous catalysts for this reason, among others) with even higher EWF values efficiently withdraw charge from aromatics and make them susceptible to addition. In a combination of two metals or semiconductors local charges are produced at the contacts which can be altered by heating or cooling them (Seebeck and Peltier thermoelectrical effects) while the perturbed π -electron systems of adsorbed aromatics can now be attacked by electrophiles like chlorine without secondary rearomatization. The now outphased insecticide lindane (γ -hexachlorocyclohexane) and its stereomers are thus produced from benzene and chlorine (also by a photochemical pathway), or cyclohexanone from H_2 addition to phenol (followed by tautomerization of cyclohexene-1-ol) while the charge taken up by PGM, Re or gold interfaces can be shuttled to an electrode also, allowing for oxidatively processing aromatics in fuel cells or removing them by catalytic oxidations. Likewise, CO adsorbed to Pt is much more readily oxidized than in the gas phase.
 - 3) If binding to a surface becomes about as strong as covalent bonds within the sorbate are, adsorbed molecules will be torn apart⁴⁶⁾ and their fragments
- 46) Within a molecular orbital treatment of chemisorption, several cases must be distinguished: if there is some diatomic molecule, removal of electrons by the adsorbing support will, as a rule, *weaken the bonds between the two atoms of the sorbate* if it is located "flat" on the surface while bonds orders might even increase

adsorbed individually (chemisorption), getting a chance to recombine forming something different from the original sorbate. Often CC bond frameworks get decomposed thereby.

This might happen on either newly created interfaces [mechanochemistry, with the new interfaces produced by grinding larger crystals (the classical case of tribochemistry⁴⁷⁾], freezing a material thereafter acting as a sorbent, growing some crystal from supersaturated solutions or gases or by vapor deposition] or such ones “cleaned” by prior thermal, photochemical or ultrasound desorptions of previous sorbates. It is pretty difficult—even when employing both many kinds of spectroscopy (surface-enhanced Raman, infrared, EELS, He or Ar atom scattering, neutron diffraction, etc.) and quantum-chemical calculations combined—to determine which of the above three effects is going to prevail or does dominate the actual reaction at a given catalytic interface, like silica or La_2O_3 . Thus, heterogeneous catalysis until now is often dismissed as a kind of “black art” (Rothenberg, 2008) in which nobody understands what actually is going on although things now are improving, and they do so because it has become feasible to get a direct look at atoms—single or conjugated—playing their games on real catalyst surfaces. This is achieved by scanning tunneling microscopy (STM; Figure 3.11a–c).

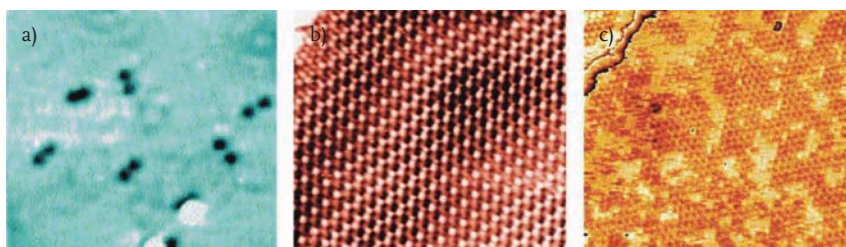


Figure 3.11 The three pictures display (from left to right): (a) eight oxygen molecules at platinum having reached different states of chemisorptions and O–O separation (the two right ones are distinctly separated, the uppermost a little bit while the others still stick together at the sorbent interface), (b) a

closed monolayer of CO molecules spread “lying flat” on Pt and (c) the effects of admitting oxygen gas to such a layer: “holes” are produced, CO molecules left behind start to migrate while CO_2 desorption is fast (<0.1 s) already at 163 K. Photos by Prof. Wintterlin, University of Munich.

when there is “vertical” adsorption (end-on), especially with NO. So CO is readily cleaved or disproportionated into C atoms (adsorbed carbide) which then can add H_2 or water, and CO_2 (Fischer–Tropsch type chemistry) while reaction pathways of NO might depend on how closely packed NO molecules are in the adlayer, eventually forcing them into some rather upright position (the same with O_2 unless for previous electron uptake separating O–O bonds).

- 47) Tribochemistry can produce both distinctly “uphill” reactions (grinding gold foils in a CO_2 atmosphere yields endothermic gold oxides Au_2O and Au_2O_3 which are difficult to obtain otherwise, besides CO and carbon black) and stunning rearrangements (Thiessen, 1971): using silicon carbide (SiC) balls in a ball mill containing nothing else but moist nitrogen will afford HCN (H taken from water, N from N_2 and C from the solid) and even several amino acids!

It allows to display surfaces and their adatoms at $\ll 1$ nm (i.e., atomic or sometimes subatomic) resolution, including real catalyst surfaces like platinum shown below. As STM (Binnig and Rohrer, 1986) does provide pieces of information on local charge distribution additionally, our ideas on heterogeneous catalysis underwent a real revolution (Ertl, 2008). An impressive, fairly comprehensible example is adsorption of CO and O₂ and mutual oxidation on platinum, which is one of the partial reactions in a three-way catalytic converter.

After a while (45 min), even an extremely tenuous CO atmosphere ($6.7 \mu\text{Pa} = 67 \text{ pbar} = 1.6 \cdot 10^9 \text{ molecules/cm}^3$) will produce a closed, complete monolayer on Pt, with C–O bond axis almost parallel to the Pt surface, producing something which looks like a tiling and where each CO bridges 2 Pt atoms. Whereas O₂ chemisorbed on Pt without any additions around will get its molecules slowly dissociated, it will not penetrate the above CO adlayer in a mixed system but react from outside oxidizing CO already adsorbed to CO₂ then readily leaving the interface as it was never stricken into (first-layer only) chemisorption.

Thus “holes” in the chemisorbate layer are produced, baring platinum, which occupy at least the area of single adsorbed CO molecules but can be much larger and will eventually be closed by adsorbing new CO molecules (the right picture Figure 3.11c is taken from an outright video of ten STM frames/s which can be viewed on the Web at www.cup.uni-muenchen.de/pc/wintterlin). Here, this reaction occurs at -110°C whereas in gas phase CO/O₂ mixture would not ignite below several hundred $^\circ\text{C}$; this massive reduction of a threshold temperature is one aspect of catalysis.

Furthermore, you need not take the electronic state (charge distribution, polarization, bond stretching) of some sorbate-sorbent system “as is” but you can alter it by electrical polarization or charge transfer due to absorbing electromagnetic radiation. The first is done simply by applying some potential, the latter by either optical or radiolytic charge transfer at a semiconductor interface (“smart people shine light on their electrodes”). One is electrochemistry,⁴⁸⁾ with primarily organic electrochemistry depending on the electrode material while the other case refers to photoelectrochemistry or radiochemically activated heterogeneous catalysis (Boris V. Spitsyn, Russian chemist).

As mentioned before and is obvious from the term, homogeneous catalysis takes place in monophasic systems, usually solutions. An example from the gas phase is the venerable lead chamber reaction, that is, air oxidation of moist SO₂ catalyzed by nitrogen oxides to yield sulfuric acid. In biology, heterogeneous catalysis is most common [solid protein enzymes (tissue materials, inclusion in membranes) operating in aqueous or lipid media], although homogeneous systems also occur [degradation of lignin (solid) in wood by exoperoxidases (solid) given away by

48) Many inorganic redox systems can be run on almost arbitrary kinds of electrodes as long as these are stable in the applied conditions (electrolyte medium, redox potential) whereas organic transformations use to succeed only at certain selected

cathode or anode materials (Weinberg and Weinberg, 1968; Kyriacou, 1994). This need not be Pt or another noble metal; often lead, nickel or cobalt provides better results and selectivities.

basidiomycete fungi mycelia (solid once again) which penetrate into wood], in biotechnology suspensions of isolated enzymes can also be run homogeneously. In environmental compartments, both homo- and heterogeneous catalysis occur. Abundant homogeneous catalysts in environmental chemistry—both the “spontaneous” and the “clean-up” brands—are nitrogen oxides in air, dissolved transition metal ions and humic matter in water, while clays and—most important for catalytic oxidations in geo- and pedochemistry— MnO_2 act as heterogeneous catalysts.

Typical applications of heterogeneous catalysis in the field of environmental engineering and technical chemistry include synthesis of ammonia from its elements N and H, the three-way catalytic converter in Otto engine cars or use of Cu/V or Cu/Mn oxides in flue gas denitrification. Homogeneous catalysis is less popular because you are to avoid catalyst carryover and eventual loss in a flowing medium, such as some flue gas stream to be cleaned. There are limiting cases, especially suspensions which link both kinds of catalysis, for example, the living sludge in a sewage treatment facility: Obviously microorganisms are “solid”, yet form catalytically active plankton as long as present in rather small concentrations (homogeneous system) while their growth (more biomass per volume unit) turns them into filterable sludge (thus, becoming heterogeneous with respect to wastewater).

3.2.5

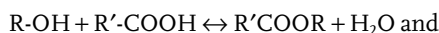
Throughflow Equilibria and How to Run a Process

3.2.5.1 Equilibrium, Equilibrium Constant and Reaction Kinetics

For analyzing chemical equilibria directly (rather than inferring them from thermodynamic data, see below), you are to give the system much time for the equilibrium to establish and then:

- Measure the heat of reaction to calculate the equilibrium constant at a given temperature (thus requires isothermic removal of reaction energy like in differential thermogravimetry; DTG) or:
- Directly analyze the equilibrium mixture, for example, by GC/MS.

The latter can be done only if the equilibrium constant k is rather close (neither much bigger nor much smaller than) to one. Two famous examples for this situation ($k \approx 1$) which are discussed in (especially older) textbooks quite commonly—and are prominently discussed for their historic role also—are the equilibria alcohol + carboxylic acid/ester + H_2O and hydrogen + iodine/hydrogen iodide according to:



respectively. The first way to determine an equilibrium of course will go the better the more energy is released or taken up (this also can be readily done in DTG

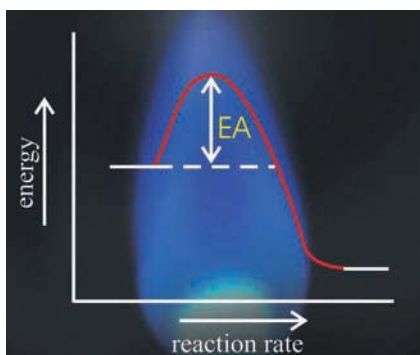


Figure 3.12 Pathways (reaction coordinate) of an exothermic reaction (the free energy of educt mixture is higher than of products). For the reaction to occur, the educt(s) must be passed across (above) the energy threshold (activation barrier; EA) which can be done

both thermally and by selective photochemical excitation. However, products need not be identical then (Woodward–Hoffmann rules). Photograph courtesy of: www.800dpi.com; scheme overlaid by the authors.

experiments on solid samples), with the equilibrium being far from order one (that is, $k \gg 1$ or $k \ll 1$). In terms of reaction kinetics, the equilibrium is given by the ratio of “forward” and “backward” reactions⁴⁹⁾ inside some closed system.

$$K = k_1/k_{-1}$$

For theory it does not matter how fast these reactions are under experimental conditions (in chemical paleontology it is quite important that certain exothermic processes like hydrolysis and racemization take geological periods of time to occur in sediments and fossils); of course, catalysts do neither shift equilibrium but just enhance rates of both forward and backward reactions in a balanced way, not altering the quotient (ratio). As stated above, reaction rates depend on both size (height) of activation barrier (see Figure 3.12) and on density/concentration of reactants (e.g., gas partial pressures).

3.2.5.2 From Equilibrium Thermodynamics into Flow Systems: Which Are the Effects by Adding and Removing Substances Steadily?

Unlike with geochemistry, kinetics do really matter when trying to clean the environment by chemical means or to avoid contamination from some technical device. The reactions must be rather fast, thus, and “genuine” equilibrium cannot

49) If there is no backward reaction, like in the irreversible and often explosive thermal decay of azides (hydrazoic acid derivatives) $R-N_3$ or $M(N_3)_x$, there is no equilibrium constant even though it might be calculated from the free energy of the reaction. Whether a reaction is actually reversible, can be seen by, for example,

isotopic exchange going on after equilibrium was attained and there is no more macroscopic change of composition over time: for example, ^{13}C -formic acid (H^{13}COOH) and ethyl ^{12}C -formate ($\text{H}^{12}\text{COOEt}$) will scramble carbon isotopes at the carboxylate position in an ethanol solution when an acid catalyst is present.

be realized as the reaction chamber cannot (!) be a closed system, requiring both inflow of pollutant-laden fluids (exhaust gases, contaminated ground-water with the reactive barrier), and removal of environmentally more benign products continuously. This, accordingly, is an open system for which, like with living beings and their continuous metabolic matter exchanges, the rules of non-equilibrium thermodynamics (throughflow system) apply.

Smoke gases from fossil-fuel power plants rush through dust filters, denitrification and desulfurization devices at some 30 m/s which is a gas stream of wind strength 11 Beaufort. If you place a denitrification plant into this gas stream without changing the cross-section, and this device is 6 m long, hence the process of denitrification (by whatever chemical process or reactant) must be (almost) completed within a fifth of one second. But this is not only demanding in terms of reaction kinetics and possibly required catalysis, but:

a steady removal and admission of reactants and products precludes chemical equilibrium to be reached. Rather, there are flow-state equilibria or, if kinetics are slow, pseudoequilibria⁵⁰⁾ which are poorly defined in thermodynamic terms. Although chemical equilibrium is not attained when removing components or intermediates or products from the reaction chamber, it can even be an advantage for the reaction to proceed to completion. There are different options for this result which is paradoxical at first glance:

- 1) The reaction may be irreversible. In environmental technology, this includes chemical reactions which produce N_2 or consume ferrate(VI) in soil or water.
- 2) Separate phases are formed which escape equilibrium by separation.
- 3) Constant removal of products, filtering off precipitates in a continuous or periodical fashion, or having gases pass through a membrane selectively (H_2 through Pd metal membranes, O_2 through polyphosphazene polymers) allows to push a reaction which actually consumes free energy into completion.

Of course, this will succeed only if the system is kept from re-establishing equilibrium ever after: a precipitate must be given no chance to re-dissolve but be removed by sludge filters, pumps and so on (corresponding separation procedures—be they chemical or mechanical—afford the “missing” free energy, by the way).

Product removal means shifting the equilibrium state toward the right (product) side exactly to those chemical species which are removed, for example, in the above case of esterification according to:

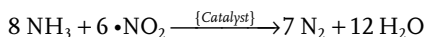
50) This corresponds to some pseudopotential in electrochemical reactions: the value of some 1.5 V vs normal hydrogen electrode (NHE) at pH 0 which is measured at an Pt electrode when combining permanganate MnO_4^- and some reduced form of Mn is not at all related to an equilibrium state which is given and can be calculated from the potential value (cf. derivation of

Pourbaix diagrams). Though not simply arbitrary, this value rather corresponds to the present polarization of the secondary electrode, making it hardly reproducible. The same holds for the sometimes stunningly high or low potentials associated with redox transformations of irreversibly reacting components like azide or hydrazine.

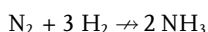
$$[\text{ester}][\text{H}_2\text{O}]/([\text{alcohol}][\text{acid}]) = k \approx 1$$

Esters are much more volatile⁵¹⁾ than alcohols or carboxylic acids as they lack H bonding even though they are larger and heavier molecules than either educt. Hence the fragrant ethyl formate (producing the flavor of arraq) can be removed by constant distillation at 50–60°C from a mixture of ethanol and formic acid steadily, allowing to convert this mixture into the ester almost completely.⁵²⁾ Irreversible chemical transformations bring about similar effects but are distinguished by no real chemical equilibrium (as the “backward” reaction channel is simply missing).

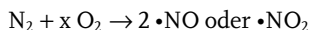
Solid phases are produced and separate, for example, during smoke gas desulfurization (here: gypsum), whereas an example of an irreversible reaction not influenced by equilibrium formation is that producing molecular dinitrogen upon denitrification by adding ammonia or urea at Cu/Mn- or Cu/V contacts according to:



which exactly is irreversible even if hydrogen would be present since neither catalyst (mixture) can promote ammonia formation from the elements (there hence is no way into the backward reaction), thus



Although there is a third conceivable competing or back reaction with O₂, namely



it is strongly exothermic at low temperatures (about 450°C), does occur only at T > 1300°C, and, being endothermic, also escapes any possible catalysis.

3.2.5.3 Nonlinear Chemical Kinetics Can Occur in Throughflow Systems

Catalyzed reactions can display really strange modes of behavior—thus dubbed “exotic” behavior (Pota and Stedman, 1994)—especially in flow conditions: there arise reaction fronts and chemical waves; and oscillations⁵³⁾ and even chemical

51) The boiling points of formic acid HCOOH, ethanol and ethyl formate HCOOC₂H₅ are some 102°C, 78°C and ca. 47°C, respectively.

52) Some part of the ester will remain dissolved in the mixture while a fraction of formic acid will decompose into water (by-product of esterification!) and CO during heating.

53) It is quite common (Eiswirth *et al.*, 1991a, 1991b) to make categories of chemical oscillations according to their occurring in conditions of continuous throughflow only or also (not besides but as an alternative) in some batch reactor. While oscillations

are also observed with enzyme reactions like glycolysis in batch systems also, these would not happen in the metabolic setting of continuous flow. Most biochemical processes, from molecules to complete organism’s metabolisms are such that oscillations can be expected to occur in batch conditions at most, if any (Fränzle and Markert, 2003).

Interestingly, while onset of oscillations in batch systems like the classical, paradigmatic Belousov–Zhabotinsky oscillator [CH-acid (malonic, cyanoacetic, citric acids, acetylacetone, etc.) + bromate + Mn³⁺ in highly acidic solutions] can be

chaos can be observed. In such oscillators, concentration levels of some intermediate—often, molecular iodine—or pH or/and redox potential of the mixture change periodically or (rarely) in a chaotic manner between two limiting values for a couple of up to hundreds of times. Using appropriate indicators {starch for iodine, pH indicators, ABTS or $[\text{Fe}(\text{phen})_3]^{2+}$ for redox states} these periodic changes translate into changes of color among two or three different states.

Equilibrium position usually is not an issue in most chemical processes operated in environmental engineering since these tend to be distinctly exothermic. An exception is enrichment (withdrawal) against some concentration gradient by reverse osmosis which requires mechanical energy (hydrostatic pressure) to be applied. Otherwise the challenge is “only” to control some readily feasible reaction in kinetic terms by either catalysis or heating, safeguarding: (i) the removal of reaction heat and (ii) avoiding the above non-linear effects on larger scales to occur (chemical wavefronts are seen in CO oxidation on three-way gas converter interfaces actually; Wennerström and Lidin, 2007).

3.2.5.4 Flow Equilibria in Biology: The Blueprint and Precondition for Biomimetic Processes

In biology, and hence biotechnological measures to be taken in environmental engineering, flow equilibria are most important, for quite a number of reasons, including:

- 1) The relative continuity of metabolic exchange by eating, breathing and excretion;
- 2) The selectivity which is buried in the fact that but some of the thermodynamically possible chemical modifications in food or other substrates are actually catalyzed by enzymes;
- 3) The control of numerous diffusion and other transport processes by means of and across membranes. Hence biological processes are also selective and likewise occur in flow equilibrium conditions.

Organisms are the classical open systems. Hence, biomimetic and bionic⁵⁴⁾ approaches are most suited to give hints for designing processes and devices in

influenced by venting off or adding elemental bromine intermediate, chemical waves are produced in thin layers by either photoexcitation or “stimulation” adding or removing some intermediate also.

- 54) Biomimetic means mimicking biological activities in their chemical (bioinorganic chemistry), dynamic (ways of propulsion, like boats with fins or ornithopters), or information-processing aspects (bolometers, magnetic sensors, ion-diffusion devices). Practical examples include all chemical (polyamide polymers like nylon are related to proteins), process (Cu-catalyzed oxidative ring cleavage of

aromatics vs laccases, monoamine oxidases) and functional features (moving around by legs, fins, flapping wings rather than rotating entities like wheels or propellers) and, perhaps most important, modes of construction (crane arms mimic long bones in inner structure). The latter two (functional and construction-related) kinds of biomimetic approaches also are called *bionics*. Eventually, in both construction/engineering and catalytic chemistry the very pathway of biological evolution by variation and selection of the fittest variety can be copied for technical purposes also (Rechenberg, 1973).

environmental engineering. Membrane reactors like those involved in both reverse osmosis (sea water desalination, water cleaning) and enzymatic sewage water treatment are very much related to working principles of human and animal kidneys. Yet, one should be aware during design that membranes and selective catalysts will direct and control dynamics in a way which is most complex also in theoretical terms, far beyond this introductory approach. While there is a detailed analysis by Eisinger *et al.* (1996) of chemical oscillations and wavefronts in a simplified three-way catalytic converter ($\text{CO} + \text{NO}$ on neat platinum) and the risks of these oscillations with respect to proper, reliable function, the works by Nicolis and Prigogine (1977) are recommended to the more specifically interested reader.

Practically, it must be asked how stable and reliable purification systems in environmental engineering could be if they get forced into some non-linear reaction regime by selective diffusion and catalysis. There can be quite different reasons for defects and poor general performance, most of them affecting the very membranes and catalyst materials, including pressure increases by boiling or gas production, excessive local heating and so on.

Nevertheless the kidney is a quite telling example of how to design a membrane-based filter system (Figure 3.13). In technical terms, it is a membrane reactor

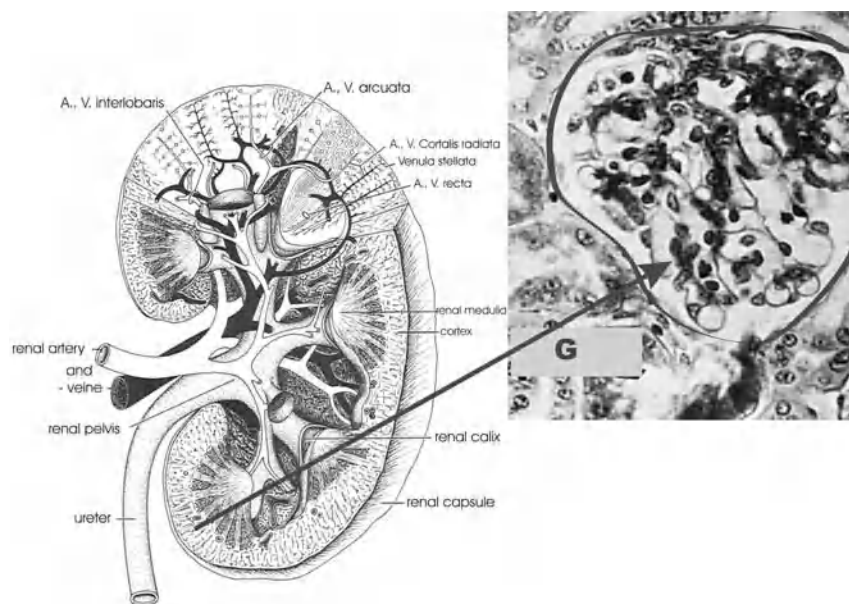


Figure 3.13 A longitudinal section through a kidney. The glomerulus G (kidney body) contains a three-layer filter membrane which, arranged in a spiral, resembles a technical membrane filter. The adjacent tubulus (beginning near bottom edge in the right figure) can re-resorb ions and organic

compounds which escaped primary filtration. Because ion transport is accomplished by consuming chemical energy and the final osmotic pressure of urine might surpass that of blood, there are similarities to inverse osmosis (after Oehlmann and Markert, 1997, modified).

which accomplishes uphill concentration of pollutants in some limited solvent (water) volume meant then to be discarded (discharged), and it does so by means of active transport, that is, by adding chemical energy to the apparatus. In the latter way the kidney differs from most technical methods to purify solvents, which use either mechanical (reverse osmosis), thermal (distillation) energy, solvent extraction or simply work by adsorption.

Besides, there are options in environmental engineering for purification along membranes which cannot or hardly be applied by biology for various reasons, like electrochemical precipitation or using mechanical pressure in reverse osmosis. Biological membranes would likewise be damaged by attempts of unpolar solvent extraction; in addition, blood hypertension is a key hazard for kidney function, rather than promoting filtration! Yet there are similarities between biochemical active transport and reverse osmosis, as between osmotic balancing by non-electrolytes rather than salts in hypersaline-adapted organisms [algae, brine shrimps, fishes like *Cyprinodon macularius* (desert pupfish) and common stickleback] and technical control of membrane separation functions in highly salt or acidic media.

During the preconcentration of primary (very diluted) urine, the kidney gets rather close to precipitating Ca^{2+} salts of certain ambient ions (sulfate $\rightarrow$ gypsum) and metabolic products like oxalate ($\rightarrow$ whewellite) or uric acids ($\rightarrow$ Ca urate) by exceeding the solution equilibrium. With either unbalanced diet or improper (pathological) kidney function, solids can form, such as kidney stones, sometimes getting considerably large. In the same way, technical membranes can be covered by salt precipitates during their purification work, which blocks further passage and renders them useless at least until they are cleaned. In addition, technical membranes can be attacked by reagents quite like those of the kidney, either blocking permeation or producing leakage through pores. In biology and toxicology, there are many kidney poisons acting in this manner, including Cd^{2+} ions, the permanent administration of which renders the kidney membrane so porous as to permit even protein molecules to pass (toxic proteinuria) while uranium salts make kidneys fail altogether.

3.2.5.5 The Hard Way into Flow Equilibrium

Up to this point, we tacitly assumed that a reaction which is to remove some product from equilibrium by phase changes attends chemical equilibrium more or less instantaneously. However, it is exactly precipitation where this assumption does not hold:

- There can be metastable, highly oversaturated solutions, especially with highly insoluble salts like barite (BaSO_4).
- Precipitation can be precluded altogether by the first forming (small or even nano-)particles adsorbing ions of like charge sign, for example, with NiS. Thus they repel each other and remain suspended; however, with pH changes or the addition of corresponding salts like ammonium acetate (a buffer), as happens at river mouths and estuaries, there may be rapid precipitation.

- The more energetic, more soluble, although less stable crystalline form of some compounds will initially precipitate if there are several (>1) different crystal structures possible for these compounds (Ostwald's rule of stages). On the one hand, the solubility of the primary may be so good⁵⁵⁾ that there will actually be no real precipitation; on the other, conversion to the stable form might take geological periods of time (e.g., CaCO_3 , aragonite toward calcite, or FeS_2 , pyrite to mackinawite).

All these effects may combine precisely in throughflow systems to produce difficulties far larger than those by "too slowly" approaching equilibria in such systems.

- 55) There may be quite substantial differences among solubility products of various metamorphs of the same substance: while the pK_i of violet Cr(III) phosphate (first to precipitate) is 17.0, the corresponding value of stable green CrPO_4 is 22.6. If one tried to remove Cr residues from wastewaters of tanneries and so on after chromate reductions by adding HPO_4^{2-} , the chromium concentration in water

would be instantly 400 000 times (!) as large as "planned" when just considering green CrPO_4 . When trying co-precipitation along Al(III) and Fe(III), the effect will be less dramatic but still exist as violet-pinkish vivianite FePO_4 —here as $(\text{Fe}_{1-x}\text{Cr}_x\text{Al}_y)\text{PO}_4$, also is the stable form of Fe(III) phosphate and hence, according to Ostwald, not the first to crystallize and fall out.

4

Specific Studies

These specific studies in environmental engineering are meant to show how problems may shift in the eyes of an engineer concerned with tackling nasty substances in technical amounts in environmental dilution states rather than processing some milligrams or grams of the pure compound with expensive purified reagents in the laboratory only. Also, we are going to discuss cases which deal with environmentally and ecotoxicologically pertinent compounds for which large-scale treatment rather than avoidance and substitution is still to be designed. For didactical reasons, the focus rests with the following kinds of agents, for example, we must consider:

- Complexation agents (ligands) which can extract heavy metal ions from sediments in certain cases and thus increase their bioavailability;
- Pharmaceuticals which withstand sewage water treatment;
- Compounds/mixtures which produce pollutants or precursors thereof when burned (S in fuels, photooxidant precursors);
- Phenomena which bring about pollutant formation, like formations of ozone and N oxides in electric discharges of various kinds.

The said compounds and methods are often applied in circumstances where many of the corresponding products will make it into the environment and cause adverse effects in it. This is why we insisted on teaching the very principles of effects and possible chemical reaction modes in environmental chemistry and technology: environmental engineering is mainly about controlling those adverse effects.

This is done for a certain reason: both chemists and engineers are trained to think along particular (chemical or technical) structures and their properties (redox potential, reactive groups, breakage failure load, resonance vibration frequencies, etc.) when musing what could happen, work or fail rather than in a purely abstract matter. All precipitation, complex formation, redox reactions or effects on (aromatic compound) reaction kinetics as described by the Hammett equation can hardly be grasped when considering a real, chemically complicated environmental medium unless these considerations deal with certain compounds. As this is due to their respective professional training, students of these disciplines live with the same limitations, if not more so. Hence the likely outcome of an

abstract treatment would be an only superficial understanding of the things which go on. Accordingly we now switch to a view on specific compounds which make their way into environment and their respective properties.

Looking on a given substance as suggested above, we are faced with properties which are either not directly obvious to the chemist or a compound which is being used and spread for certain favorable properties and which turns out to display others which are neither apparent nor wanted. But it must be taken into account when judging whether further use is acceptable or how to dispose of the compound if it proves to detrimental. Necessarily one must ask how to avoid the respective negative effects. Options include: (i) the destruction/conversion of the pollutant, (ii) withholding it from the environment by some filter device or (iii) outright substitution. Sometimes, like with CO₂ sequestration, all the cited options are viable, that is, given certain boundary conditions, the different physical, chemical and biotechnological approaches compete with each other in a way for the optimum solution. Then, these approaches, their respective principles and limitations have to be discussed in a comparative way. Sometimes it is still impossible to predict or guess which method will represent the optimal one to tackle some problem, while technical progress here or there can rapidly change relative judgments on such competing methods. Besides their being interesting or most original, this may be another reason to quote approaches in some detail which not yet made it into large-scale applications anywhere in the world.

Hence, most case studies look all the way from applications and by-effects and properties of some compounds via defining the environmental and—if any—ecotoxicological problems associated with it in either environmental compartment or certain ecosystem¹⁾ which suggest or necessitate remediation, and sometimes suggest certain methods to be applied for purposes of removal extraction. Then practical methods are discussed, including the economic aspects of running the given device (how many € or \$ it will take to gather, separate and inactivate 1 kg of potential pollutant?). Finally, there is a short “résumé” in the methods to be preferred given the present situation, the state of the art and the problem still to be addressed.

4.1

Atmosphere

4.1.1

Bioindication and Biomonitoring

Innovative, for monitoring and controlling environmental situations, means: the case of atmospheric emission surveillance.²⁾

1) Factors like very low or high volatility can withhold a chemical from getting into it, very nonpolar substances strongly adsorb onto soil and other sediments while acids, phosphates, or certain organics exchange for carbonate in corals, bones, clam shells

and the like, altering structures and properties.

2) According to Markert (2007), Markert and Wünschmann (2011), Markert, Breure and Zechmeister (2003b) and Markert *et al.* (2008, 2011).

4.1.1.1 The Problem

All the environmental compartments air, water, soil and the biocenoses associated with them are considerably influenced by a larger number of both biotic and abiotic factors (Ellenberg, Mayer and Schauer mann, 1986; Haber, 2009; WHO, 1996; Zhu and Jones, 2010). Owing to an increasing extent of industrial activities, the environment is also influenced by chemical pollutants. This diverse group of potentially hazardous substances contains a larger number of organic compounds as well as heavy metals (e.g., mercury and tin), so-called semi-metals (e.g., arsenic and antimony) and organometal compounds (like tributyl tin). Once they accumulate in the soil, ground water or organisms, drawbacks for certain members of a trophic chain may become unpredictable, yet grave (Adriano, 1992; Baker and Brooks, 1989; França *et al.*, 2007; Kashulina, de Caritat and Reimann, 1998; Markert *et al.*, 2003a,b; Rauch, 2010; Reimann *et al.*, 1999; Schmull and Hauck, 2003; Wang *et al.*, 2010, 2011).

Ancient high cultures already used metals to an extent, the emissions from which can be detected globally by corresponding depositions in, for example, Greenlandic ice cores. During the past 150 years, however, anthropogenic emissions grew so large that negative effects on man and his environment were no longer restricted to the regional surroundings of the emission sites.

Accumulation being a slow, inconspicuous process which, however, causes a likewise slow damage to living organisms requires a meticulous and constant surveillance of the deposition of heavy metals (likewise organic compounds) and their impacts on living nature.

Emissions into the atmosphere are often monitored by means of deposition collectors whereas in aquatic monitoring a sampling—not continuous but intermittent—of water samples is employed.

There are elegant though indirect methods to obtain data on the existence, distribution and effects of pollutants, namely, bioindication and biomonitoring. These methods make use of the capacity of organisms to signify the presence of pollutants over either shorter or longer periods of time. Intensive studies of these bioindications and biomonitoring have been done by (among others) the following colleagues: Adamo *et al.*, 2003; Bargagli, 1998; Bargagli *et al.*, 2002; Carreras, Gudino and Pignata, 1998; Chettri *et al.*, 1997; Chiarenzelli *et al.*, 2001; Conti and Cecchetti, 2001; Culicov and Yurukova, 2006; Freitas *et al.*, 2007a, 2007b; Freitas *et al.*, 2006; Frontasyeva *et al.*, 2004; Galuzka, 2005; Haas, Bailey and Purvis, 1998; Hempel *et al.*, 2008; Lee and Tallis, 1973; Hauck, Mulack and Paul, 2002; Klos *et al.*, 2010; Loppi and Bonini, 2000; Loppi, Giomarelli and Bargagli, 1999; Marcovecchio and Ferrer, 2005; Markert and Wünschmann, 2011; Markert, Breure and Zechmeister, 2003a, 2003b; Markert *et al.*, 2010; Ozturk *et al.*, 2008; Pesch, Schmidt and Schroeder, 2009; Pignata *et al.*, 2002; Pla *et al.*, 2009; Saiki *et al.*, 2003; Seaward, 2006; Senhou *et al.*, 2002; Smadis *et al.*, 2004; Szczepaniak and Biziuk, 2003; Zechmeister *et al.*, 2006; Vutchkov, 2001; Wolterbeek, 2002; Wolterbeek *et al.*, 2003, 2010.

Because bioindicators or biomonitors integrate the environmental burdens (by chemicals) over the time of experiment at their sites, short-term variations are canceled out. As compared to “conventional” means of measuring emissions,

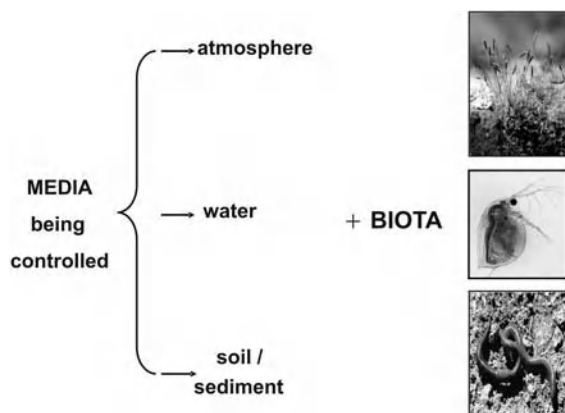


Figure 4.1 Environmental media and their bioindication using various living organisms, for example, mosses, daphnia, earthworms (Markert, 2008).

doing bioindication or biomonitoring involves much less expenditure in both personnel and apparatus than, for example, running a deposition sampler. Hence bioindicators can be employed throughout large areas provided the organisms are sufficiently far-spread and abundant, enabling investigations to cover entire countries or even continents which could be done otherwise only if accepting very high demands of work and money.

Using one or several (different) organisms for the purposes of estimating environmental burdens (Figure 4.1) brings about yet another advantage: beyond statements on the very organism which is embedded in some ecological niche within an ecosystem, the analytical data obtained on it can be integrated into a more comprehensive biological system. Thus beyond the very bioindicator ecologically relevant statements are possible on larger parts of the biocenosis due to the biotic interactions which interconnect them, unlike when using direct physico-chemical methods.

4.1.1.2 Definitions

Markert, Oehlmann and Roth (1997) and Markert (2007) gave an exact and meanwhile generally valid definition to discern among bioindication and biomonitoring:

- *Bioindicators* are organisms or communities of organisms whose content of certain elements or compounds and/or whose morphological, histological or cellular structure, metabolic-biochemical processes, behavior or population structure(s), including changes in these parameters, supply information on the *quality* of the environment or the nature of environment changes. Bioindication compares *relative data* of information (e.g., on contamination) to each other.

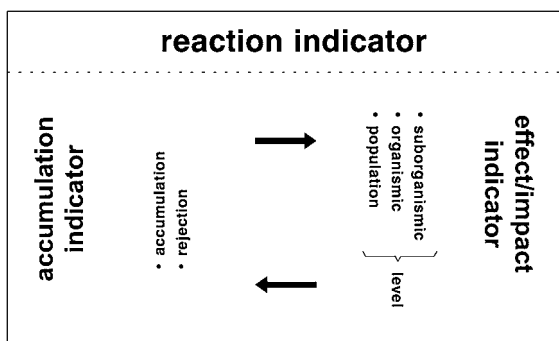


Figure 4.2 Illustration of the terms reaction, accumulation and effect/impact indicator (Markert, Oehlmann and Roth, 1997).

- *Biomonitors* are organisms or communities of organisms whose content of certain elements or compounds and/or whose morphological, histological or cellular structure, metabolic-biochemical processes, behavior or population structure(s), including changes in these parameters, supply information on the *quantitative aspects* of the quality of the environment or the nature of environment changes. Biomonitoring compares *absolute data* (e.g., on contamination) to each other.

We speak of *active* bioindication (biomonitoring) when bioindicators (biomonitors) bred in laboratories are exposed in a standardized form in the field for a defined period of time. At the end of this exposure time the reactions provoked are recorded or the xenobiotics taken up by the organism are analyzed. In the case of *passive* biomonitoring, organisms already occurring naturally in the ecosystem are examined for their reactions. This classification of organisms (or communities of these) is according to their “origin”.

A classification of organisms (or communities of these) according to their “mode of action” is as follows (Figure 4.2): *Accumulation* indicators/monitors are organisms that accumulate one or more elements and/or compounds from their environment. *Effect* or *impact* indicators/monitors are organisms that demonstrate specific or unspecific effects in response to exposure to a certain element or compound or a number of substances. Such effects may include changes in their morphological, histological or cellular structure, their metabolic-biochemical processes, their behavior or their population structure. In general the term “reaction indicator” also includes accumulation indicators/monitors and effect or impact indicators/monitors as described above.

When studying accumulation processes it would seem useful to distinguish between the paths by which organisms take up elements/compounds. Various mechanisms contribute to overall accumulation (*bioaccumulation*), depending on the species-related interactions between the indicators/monitors and their biotic and abiotic environment (Markert, Oehlmann and Roth, 1997):

- *Biomagnification* is the term used for absorption of the substances from nutrients via the epithelia of the intestines. It is therefore limited to heterotrophic organisms and is the most significant contamination pathway for many land animals except in the case of metals that form highly volatile compounds (e.g., Hg, As) and are taken up through the respiratory organs, (e.g., trachea, lungs).
- *Bioconcentration* means the direct uptake of the substances concerned from the surrounding media, that is, the physical environment, through tissues or organs (including the respiratory organs). Besides plants, that can only take up substances in this way (mainly through roots or leaves), bioconcentration plays a major role in aquatic animals. The same may also apply to soil invertebrates with a low degree of solarization when they come into contact with the water in the soil.

Besides the classic floristic, faunal and biocenotic investigations that primarily record rather unspecific reactions to pollutant exposure at higher organizational levels of the biological system, various newer methods have been introduced as instruments of bioindication. Most of these are biomarkers and biosensors (according to Markert, Oehlmann and Roth, 1997):

- *Biomarkers* are measurable biological parameters at the suborganismic (genetic, enzymatic, physiological, morphological) level in which structural or functional changes indicate environmental influences in general and the action of pollutants in particular in qualitative and sometimes also in quantitative terms. Examples: enzyme or substrate induction of cytochrome P-450 and other Phase I enzymes by various halogenated hydrocarbons; the incidence of forms of industrial melanism as markers for air pollution; tanning of the human skin caused by UV radiation; changes in the morphological, histological or ultrastructure of organisms or monitor organs (e.g., liver, thymus, testicles) following exposure to pollutants.
- A *biosensor* is a measuring device that produces a signal in proportion to the concentration of a defined group of substances through a suitable combination of a selective biological system, for example, enzyme, antibody, membrane, organelle, cell or tissue, and a physical transmission device (e.g., potentiometric or amperometric electrode, optical or optoelectronic receiver). Examples: toxiguard bacterial toximeter; EuCyano bacterial electrode. Biotest (bioassay): routine toxicological-pharmacological procedure for testing the effects of agents (environmental chemicals, pharmaceuticals) on organisms, usually in the laboratory but occasionally in the field, under standardized conditions (with respect to biotic or abiotic factors). In the broader sense this definition covers cell and tissue cultures when used for testing purposes, enzyme tests and tests using microorganisms, plants and animals in the form of single-species or multi-species procedures in model ecological systems (e.g., microcosms and mesocosms). In the narrower sense the term only covers single-species and model system tests, while the other procedures may be called suborganismic tests. Bioassays use certain biomarkers or –less often– specific biosensors and

can be used in bioindication or biomonitoring. Section 1.4.2.3 provides an example of a biotest design.

With regard to genetic and non-genetic adaptation of organisms and communities to environmental stress we have to differentiate between the terms tolerance, resistance and sensitivity:

- *Tolerance* (Oehlmann and Markert, 1997) means a desired resistance of an organism or community to unfavorable abiotic (climate, radiation, pollutants) or biotic factors (parasites, pathogens), where adaptive physiological changes (e.g., enzyme induction, immune response) can be observed.
- *Resistance*, unlike tolerance, is a genetically derived ability to withstand stress (Oehlmann and Markert, 1997). This means that all tolerant organisms are resistant, but not all resistant organisms are tolerant. However, in ecotoxicology the dividing line between tolerance and resistance is not always so clear. For example, the phenomenon of pollution induced community tolerance (PICT) is described as the phenomenon of community shifts toward more tolerant communities when contaminants are present. It can occur as a result of genetic or physiological adaptation within species or populations, or through the replacement of sensitive organisms by more resistant organisms (Blanck, Wängberg and Molander, 1988; Rutgers *et al.*, 1998).
- *Sensitivity* of an organism or a community means its susceptibility to biotic or abiotic change. Sensitivity is low if the tolerance or resistance to an environmental stressor is high, and sensitivity is high if the tolerance or resistance is low.

4.1.1.3 Using Plants as Bioindicators/Biomonitorors

Because of an unfavorable location, many plants have developed the ability to enrich high concentrations of individual elements, often regardless of whether these elements are physiologically useful or not. These plants are called accumulators. With respect to biomonitoring there should be a correlation between the environmental concentration of a pollutant to be observed and the content in the organism proper. A linear, indicative interrelation of both measure values has not been found so far for any organism. The concentration ranges which might be interesting for bioindication and biomonitoring showed very small “measuring ranges” (black bars) in accumulator and excluder organisms (Figure 4.3).

For example, regardless of the amount of element in the soil, some Ericaceae have a high concentration of manganese, and beeches have a high level of zinc. The accumulative behavior, which may have genetically predetermined origins rather than ones determined by locations, makes it possible to chemically fingerprint a very wide variety of types of plant. In the future, this might lead to the chemical characterization, and therefore the systematization, of individual plant types which could provide information about evolutionary connections on a phytosociological level. A rejection, or reduced uptake of individual elements, occurs less frequently than does an accumulation of elements, but rejection behav-

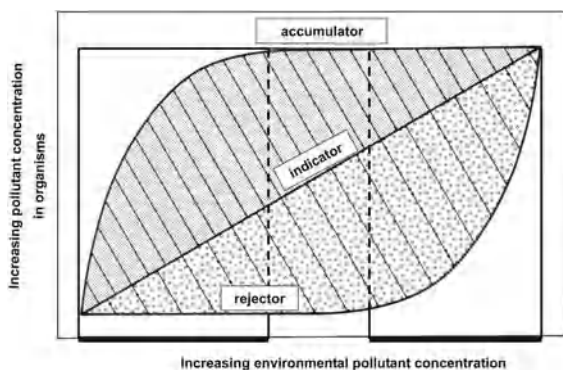


Figure 4.3 Differing uptake activities in living organisms as a function of the substrate concentration (Markert, Oehlmann and Roth, 1997, according to Baker, 1981).

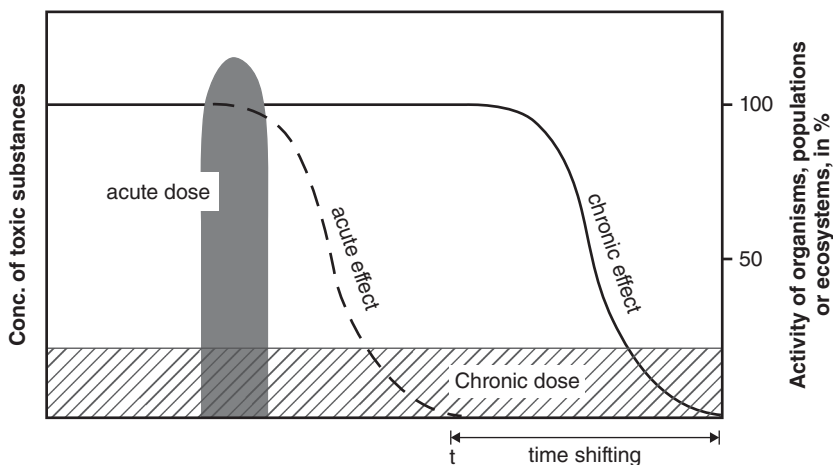


Figure 4.4 Comparison of effect of acute and chronic doses of toxic substances on living systems (Markert, 1996).

ior has been demonstrated for numerous plant species. The reduction in concentration of an element in an organism can be the result of a complete or a partial exclusion. For example, bacteria, algae and higher plants contain populations which are resistant to heavy metals and which can reduce considerably the uptake of heavy metals by excreting mucilaginous substances or by changing their cell walls.

In the context of activity studies, and especially in toxicity monitoring, generally one must differentiate between acute and chronic working models. As is shown in Figure 4.4, the acute delivery of a substance is usually followed by a direct,

short-term effect on the organism or the population. These types of toxic effects are relatively easy to generate experimentally in the laboratory by adding different substances to the test organisms. However, it is more difficult to investigate the chronic effects of a substance, meaning the subthreshold, long-term application of a substance which only shows an effect (usually a toxic one) after lengthy constant uptake. These mechanisms of chronic activities are considerably more difficult to study because all other values and parameters which could influence the test organism have to be kept constant over a considerable period of time. Often the chronic effect of substance differs from an acute effect only by its chronologically displaced occurrence. Thus, the chronic effect usually only creeps along, and so in reality it is often recognized too late.

In addition to microorganisms, fungi, algae, mosses, lichens, ferns and higher plants (examples are described in Markert, Breure and Zechmeister, 2003a) and animals can be used as bioindicators and biomonitors. In comparison to plants, animals have generally developed a greater arsenal of stress-coping mechanisms; in addition, non-sessile animals can avoid a certain number of threatening environmental or anthropogenic stressors by virtue of their mobility or motility (Fränzle, 2003). Owing to the generally higher sensitivity of aquatic animals to xenobiotics in comparison to that of terrestrial organisms they play a major role in acute, subchronic and chronic tests. Under field conditions inquiries into distribution patterns and the different for organotropic accumulation of xenobiotics are the major fields of interest in various bioindicative/biomonitoric approaches (Fränzle, 2003). Some animal groups representing indicative qualities are given in Markert *et al.*, (2003a). The possible integrative relation of atmospheric element pollution, soil samples, stomach content and tissue and organs of rats in a specific study area is given by Wünschmann *et al.* (2001, 2002). A more general investigation of bioindicative moss monitoring results to human health is given in Figure 4.10. The results of bioindicative studies of humans is manifold. For example, Wünschmann *et al.* (2004, 2008) gave impressive results on the relation of chemical elements to nutritional intake, human milk and transfer of the milk to babies. In these investigation it could be clearly demonstrated that human milk cannot be used as bioindicator/biomonitor for the heavy metal pollution status of the environment (Wünschmann, 2006; Wünschmann *et al.*, 2008). Other stimulating examples of bioindication and biomonitoring studies for controlling organic pollutants are given among others in Schwarz and Jonas (1997).

In addition, some requirements of an “acceptable” bioindicator/biomonitor are given in Figure 4.5.

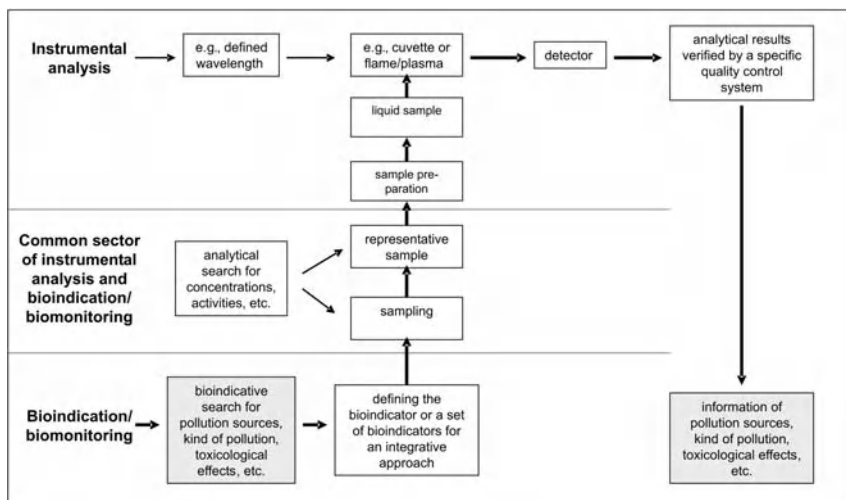
In Figure 4.5 the requirements for a bioindicator are called “simple”. But each location in the world is characterized by specific conditions of climate and living conditions. Therefore it is extremely difficult to find species or group of species which are working in the common sense of a bioindicator or biomonitor as given in the requirements of Figure 4.5 on a global level. Today, they still do not seem available. Therefore for each region, each selected indicator has to be handled with care and the experience of the scientists.

Common paradigm

- high abundance (frequency)
 - widespread (global)
 - easy identifiability
 - easy availability
 - analytical ability
- accumulation of pollutants

As an example, mosses

- primitive morphology
 - without cuticle
 - without roots
- without water conducting system
- accumulation of pollutants
 - wide distribution
 - easy to collect

Figure 4.5 “Simple” requirements for bioindicators/biomonitors.**Figure 4.6** Comparison of measurements performed by spectrometers and bioindicators/biomonitors. In practice, instrumental measurements are often an integral part of bioindication and

biomonitoring methods (Markert, Breure and Zechmeister, 2003b). A full instrumental flow chart for instrumental chemical analysis of environmental samples can be found in Markert (1996).

4.1.1.4 Comparison of Instrumental Measurements and the Use of Bioindicators with Respect to Harmonization and Quality Control

In Figure 4.6 a rough comparison is made in between instrumental methods used in the laboratory and biotechniques involving the application of bioindicators or biomonitors. Common problems are related to a representative sampling procedure which can introduce an error up to 1000% if general rules of representative

collection of the measuring samples are not taken under strong consideration (Markert, 1996). It must be clearly stated that instrumental measuring techniques are often an integrated part of bioindication, especially when considering the parameter under investigation, for example, the concentration of a trace metal. In both (instrumental and biotechniques) the sampling procedure is the essential part of the overall procedure. The sampling procedure has to be evaluated in between all (international) participants—at least those involved in the actual investigation—to obtain comparability.

In the same way as the sampling procedure for instrumental measurements and biotechniques have to be under control, terms of precision (reproducibility) and accuracy (the “true” value) have to be checked with strict standards during the overall monitoring procedure. We will not go in detail in this article, but methods to observe precision and accuracy can be obtained in all textbooks of analytical sciences (see, e.g., Kramer, 2006; Markert, 1996; Markert, Breure and Zechmeister, 2003b; Namiesnik and Szefer, 2009; Quevauviller and Maier, 1999; Quevauviller *et al.*, 2005) and in detail in Section 1.4.1.3 of this volume. Basically, two methods are now used to check the accuracy of analytical results:

- 1) The use of certified standard reference materials (commercially available samples with a certified content of the compound (e.g., a trace metal) to be measured and a matrix similar to the original samples to be measured in the laboratory.
- 2) The use of independent analytical procedures.

4.1.1.5 Examples of Bioindication/Biomonitoring: Controlling the Atmospheric Deposition of Chemical Elements by Using Mosses and Spanish “Moss” (*Tillandsia usneoides*)

Mosses as Bioindicators/Biomonitors for Controlling the Atmospheric Deposition of Chemical Elements Mosses are suited for this corresponding work as they lack a cuticular interface. In higher plants, the cuticle limits evaporation, protecting plants against drought. Further, the cuticle is an obstacle to the uptake of water and salts dissolved in it via the surface of a plant. Because there is no cuticle, mosses can directly take up water and minerals required for growth via their leaf surfaces and thus do need neither “genuine” (i.e., mineral-absorbing) roots nor a water conduction organ system. Thus the “primitive” structure of mosses as compared to more differentiated vascular landborne plants becomes a distinct advantage in pollutant level observations, with the pollutants likewise taken up directly through the surface unprotected by a cuticle.

In addition to lacking a cuticle, mosses are distinguished by a rather large resistance toward enhanced levels of various anthropogenic air pollutants, permitting their use also in polluted areas. With many species being far-spread (living in quite different regions), larger regions can be monitored using a given species. Owing to their large surface:volume ratio, mosses will readily accumulate elements. When transferred into the plant, pollutants get bound to cell walls. Thus

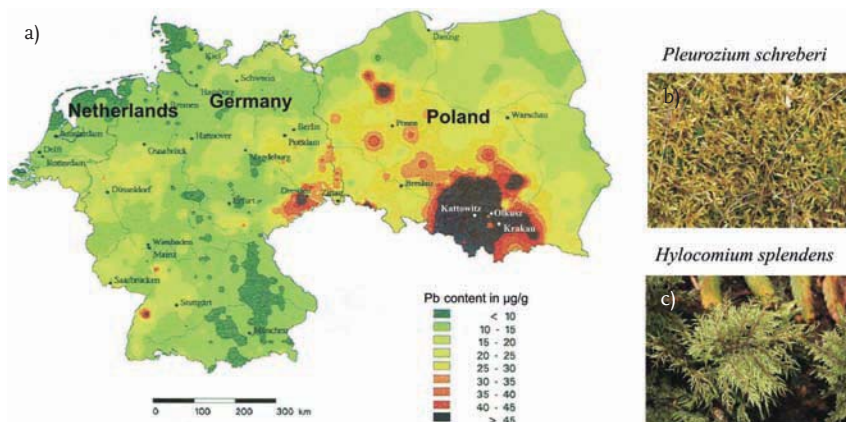


Figure 4.7 (a) This map gives Pb contents in moss species from different countries (Netherlands, Germany, Poland), using moss samples taken during 1990–1992 (Herpin *et al.*, 1996). (b, c) Mosses [only two moss species of a total of four of the overall

European program are shown as examples: *Pleurozium schreberi* (b) and *Hylocomium splendens* (c)] are bioindicators/biomonitors for controlling the atmospheric deposition of different chemical elements. (b, c) Courtesy of: wikipedia.

mosses accumulate substances throughout the entire period of vegetation growth, providing information on an averaged pollution situation integrated along the period of growth. Thus mosses are perfectly suited for monitoring pollution which is due to atmospheric deposition.

The results from chemical analysis are converted into multi-color maps of pollution using geographic information systems (GIS), providing maps such as that for lead (moss samples from 1990–1992, Figure 4.7).

As final output of above investigations bioindication results compare relative (analytical) data of (element) concentrations given by bioindicator species (mosses). In this example the mosses are represented by different locations around Middle Europe. Same can be done by using bioindicators to get an impression on behavior of chemicals by time. As example is given for Pb in mosses (*Polytrichum formosum*) collected over some years.

The characterization of typical summer/winter oscillations of Pb (and other elements given in Markert and Weckert, 1993, 1994) can be explained by a dilution effect during biomass production during the spring and summer months, which clearly explains the maximum concentrations of lead found in the winter months and lowest concentrations found in the summer months (graph in Figure 4.8). As a result of lower emission rates the concentrations for lead decreased in the time period from 1985 to 1992. This ranged from 0.2 to 0.005 mmol/kg, that is, a four-fold decrease of the original value. In addition a reduction of the yearly amplitude can be manifested. The minimum values of lead in Figure 4.8 should be noted. The lowest value was 0.01 mmol/kg, a figure which then (summer 1988) had not yet been reached. The reason for this was probably the opening of the Berlin Wall

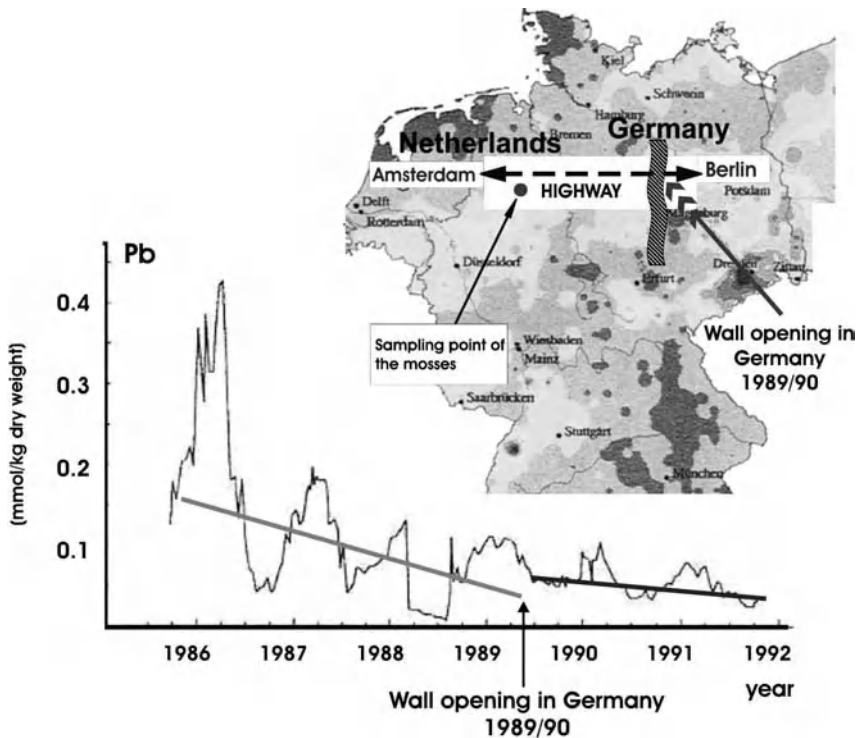


Figure 4.8 Decrease in Pb concentration in the moss *Polytrichum formosum* near Osnabrück (Germany) after regular sampling (two-week intervals) close to the highway between Berlin and Amsterdam. The seasonal

variations can be explained by the dilution effect during biomass production of *Polytrichum formosum* at the beginning of the vegetation period (Markert and Weckert, 1993, 1994).

in 1989 (Germany), as the biomonitor study site was no more than 200 m away from the highway. Consequently, it may be assumed that these increased lead concentrations were a result of automobile emissions. After the fall of the wall in 1989/1990 the ex-East Germans bought (cheap) cars which required leaded petrol. Thus the amount of leaded petrol used increased and hence also the emissions of lead. These emissions are directly correlated with the much frequented (by “eastern” cars) traffic routes as represented by the highways 2 and 30 between Berlin and Amsterdam (Markert and Weckert, 1994). From a statistical point of view (Figure 4.8) the slopes of lead concentrations before and after November 1989 increased from -0.042 to -0.017 , which can be explained by the higher lead input during this period.

For quantitative results for transferring bioindicative into biomonitoring data the values can be converted into quantitative deposition rates for chemical elements found in mosses using the formula:

$$D = c \cdot \frac{A}{E_x}$$

Where D = estimated deposition, c = measured concentration in moss, A = biomass increase/year according to Zechmeister (1997) and E = efficiency factor of uptake by Berg, Røyset and Steinnes (1995). The unit of D is given in $\mu\text{g}/\text{m}^2$ per year. Wappelhorst (1999), for example, examined the deposition of different elements via mosses in the Euroregion Neisse (ERN, East Germany, a crossbordering region in between Czech Republic, Germany and Poland) in the years 1995 and 1996 as well as in Austria (Table 4.1).

The obtained element data from the moss monitoring species *Polytrichum formosum* and *Pleurozium schreberi* served further on as basis for determining those elements in the deposited material that promote the occurrence of disease. This was done by correlating the figures for the various diseases with the appropriate element concentrations in the mosses (Wappelhorst *et al.*, 2000). As can be seen in Figure 4.9 indications were found that a connection exists between the thallium content of mosses and the occurrence of cardiovascular disease. Similar results of an expected relation can be found in between Ce, Fe, Ga and Ge levels in the moss and the incidence of diseases of respiratory system.

The general (scientific) problems of comparing moss (element) data with effects to human diseases are manifold, for sure. Figure 4.10 clearly represents that it should make not much real sense to compare these data to each other. A moss represents an immobile lower plant growing in an environment which has fully other (chemical) influences as humans. Human life is influenced, for example, by different forms of living locations represented by their time spent at work, in their flat or during “free” time. Or, for sure, there is an extreme influence of nutrition, possible intake of medicine, use of cosmetics and so on in comparison to mosses. But there can be some (speculative scientific) assumptions of the comparabilities of “atmospheric influences” between mosses and humans which are related to following observations (according to Wappelhorst *et al.*, 2000): air-borne pollutants are inhaled by man and chiefly cause chronic diseases of the upper and lower respiratory tract. At high concentrations they may cause acute disorders. After inhalation the various components may have synergistic effects, with the result that their overall impact is greater than the sum of the individual substances (Berenbaum, 1995; Spurny, 1993). The substances entering the lungs may be taken up by the blood and metabolized. Air pollutants are said to be responsible for 1–5% of all additional cases of cancer (Doll and Peto, 1981) and, according to some estimates, 11–21% of all cases of lung cancer are caused by air pollution (Karch and Schneiderman, 1981). Both Doll and Peto (1981) and Karch and Schneiderman (1981) investigated the health hazard resulting from the total aerosol of the atmosphere (Wappelhorst *et al.*, 2000).

An investigation into the effects of atmospheric pollution on individuals over large areas involves the collection of data throughout the region (Wappelhorst *et al.*, 2000). Bioindication and biomonitoring are excellent means of doing this. Such an approach was done by Cislighi and Nimis (1997) in a study comparing

Table 4.1 Annual surface deposition ($\mu\text{g}/\text{m}^2$) in the Euroregion Neisse (ERN; East Germany) in 1995 and 1996 and in Austria in 1995, specifying the minimum and maximum surface deposition in the Austrian federal states (Wappelhorst, 1999).

Element	Cd	Co	Cr	Cu	Fe	Mo	Ni	Pb	V	Zn
ERN 1995	130	2300	450	4200	200 000	89	640	2100	910	15 000
ERN 1996	79	910	230	3400	140 000	52	390	1700	680	10 000
Austria 1995	52	37	150	1400	98 000	87	370	1300	370	71 000
Min.–max.	41–70	35–42	120–230	1200–1600	81 000–350 000	68–250	290–750	1000–15 00	290–940	6100–10 000

Austrian data from Zechmeister (1997).

Pleurozium schreberi

ICD 401-405: Hypertony and blood high pressure
- by higher TI concentrations?

age	55-60	60-65	65-70	70-75	75-80	80-85	>85
Be	-0.18	-0.12	-0.03	-0.12	-0.05	-0.10	-0.05
Bi	0.20	0.59	0.76	0.69	0.81	0.82	0.86
Cs	0.42	0.76	0.85	0.84	0.90	0.94	0.92
Mn	-0.09	-0.36	-0.57	-0.48	-0.60	-0.63	-0.71
Na	0.36	0.06	-0.25	-0.12	-0.31	-0.36	-0.49
TI	0.44	0.81	0.96	0.92	0.98	0.99	0.99

Figure 4.9 Coefficients of correlation between the incidence of essential and secondary hypertension [International Statistical Classification of Diseases (ICD) 401–405] and element concentrations in *Pleurozium schreberi* in the years 1993–1997, broken down according to age groups. Significant correlation coefficients are printed in bold (Wappelhorst *et al.*, 2000).

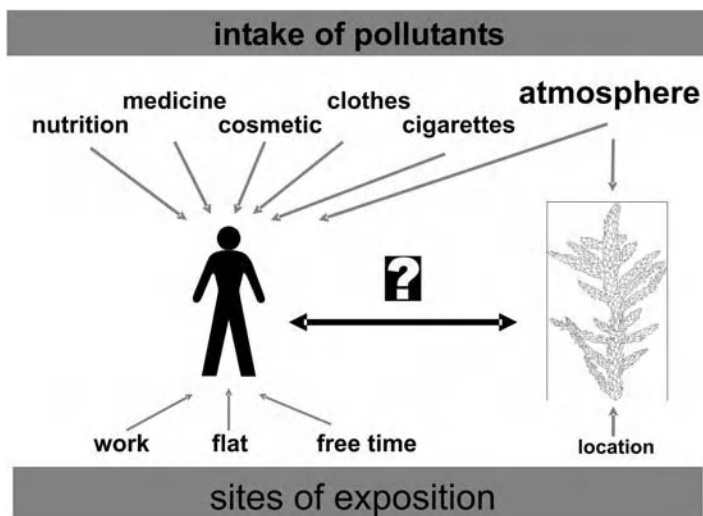


Figure 4.10 Paths by which pollutants are taken in by human beings and moss. Unlike mosses, human beings are exposed to pollutants in numerous places and take up substances in several routes (Wappelhorst *et al.*, 2000).

mortality from various pulmonary diseases with a biodiversity index for lichens. High correlation coefficients were found between the index and the number of deaths from lung cancer. However, no direct conclusions were drawn in respect to individual chemical elements or organic compounds (Wappelhorst *et al.*, 2000).

Because most of the above investigations have been done without the influence and advice of medical doctors, these results have to be discussed further on in a

interdisciplinary manner, as it is required in the multi-markered bioindication concept (MMBC) of Section 4.1.1.6 and Figure 4.13.

Today comparable investigations of calculating a relationship of bioindicators used and diseases can be found in different nations of the world using especially lower plants as bioindicator species. For example, in Europe there are intensive working groups around Carmo Freitas of the Instituto Tecnológico e Nuclear (ITN; Sacavem, Portugal) and Bert Wolterbeek from the TU (Delft, The Netherlands). Both scientific groups are working strong together on airborne chemical elements and implications on human health and accumulation in lichens. For example they are using lichen monitoring to study an association of respiratory diseases in Lisbon (Portugal) basic school children with traffic emitted components [see papers of Freitas and Wolterbeek *et al.* during the Fifth International Workshop on Biomonitoring of Atmospheric Pollution, in Buenos Aires in 2009 (Freitas *et al.*, 2010), and the earlier BIOMAP conferences].

Spanish Moss as Bioindicators for Controlling the Atmospheric Deposition of Chemical Elements in Megacities³⁾ The number of towns⁴⁾ steadily increases globally. Some 200 years ago (in 1800) just 25% of German population lived in cities, as opposed to 75% in rural environments, while in 2005 the population share of German towns had increased to 85%. Similar developments are observed in all industrialized countries: as of 2005, the corresponding shares of urban populations were 61% in Ireland, a stunning 97% in Belgium, 77% in France, 90% in the United Kingdom, 66% in Japan, 73% in Russia and 81% in the United States. The increase in number and average population was largest in megacities [megacities are not subject to an unequivocal definition but usually the minimum is taken to be three mio. inhabitants (about the size of Rome, Chicago, Kiev, Montreal, Berlin or Sydney), but sometimes higher limits of five, eight, or even ten mio. inhabitants are taken]. Anyway, we will count Mexico City (23 millions), São Paulo (20 millions), Buenos Aires (15 millions) and Santiago de Chile (5 millions) among the megacities.

Atmospheric burdens are enormous in megacities. If pregnant women are exposed to CO, the fetus will be harmed. Likewise, experts agree that car exhaust gases strongly damage children's health, including effects on behavior and psychosocial development (Chelala, 2010).

In Mexico City, which is notorious for air pollution (at a total of >4.5 mio t/year of hazardous substance inputs), also children are exposed, with authorities keeping them from attending school if the extent of pollution in town is particularly high.

3) According to Markert *et al.* (2011).

4) The terms "town" and "city" are not given a consistent legal definition by administration rules, at least so far as number of inhabitants is concerned (in central Europe, there are rather many "towns" <1000 inhabitants, while in developing countries there may be settlements of >50 000 lacking both the legal status of "town" and corresponding infrastructures). For our

purposes, a town rather is a centralized settlement with clear-cut edges toward the (rural, desert, etc.) environment which maintains an administrative and support infrastructure of its own and is connected to traffic by intersecting traffic ways within. Given these structural, rather than administrative features, almost every central settlement can be considered a town.

Mexico City is not an exception; about the same holds for almost all large cities in the Western hemisphere but also in Chinese cities, Lagos in Nigeria, in Tehran (the capital of Iran) and others.

Due to high levels of atmospheric pollutants, inhabitants of Santiago de Chile struggle with chronic respiratory diseases. There, pollutants stay airborne longer than elsewhere and hence accumulate due to topographical and climate peculiarities, with Santiago “sandwiched” in between the (Pacific) ocean and the nearby Andean mountains.

Nor does Buenos Aires escape these problems. Due to both pollutant and noise emissions, it became one of the most polluted cities in the world.

In terms of extent and hazards, air pollution competes against other forms of pollution coming from waste materials, including pesticide residues and toxic industrial wastes. In Santiago de Chile, some 300 million m³ of untreated sewage water are estimated to pour into the two rivers and the main watering (!) channel of this metropolis.

In the past 10 years more and more activities were undertaken to transfer the bioindication method into the pollution control observations of megacities. In the following we would like to report on results for São Paulo (Figueiredo *et al.*, 2001, 2007), the biggest megacity of Brazil, having around 20 million inhabitants. For this reason *Tillandsia usneoides* L. (Figure 4.11), an epiphytic bromeliad plant,



Figure 4.11 Spanish moss (*Tillandsia usneoides* L.) as bioindicator for controlling the atmospheric pollution in megacities, for example, in São Paulo, Brazil (Figueiredo *et al.*, 2001, 2007).

was chosen, because this plant is able to absorb water and nutrients directly from the air.

Five consecutive transplantation experiments (8 weeks each) were performed at 10 sites in the city, submitted to different sources of air pollution (industrial, vehicular), using plants collected from an unpolluted area. After exposure, trace metals were analyzed in the plant by instrumental neutron activation analysis. Distribution maps were drawn, which demonstrate that traffic-related elements such as Zn (and Ba, not given in Figure 4.12) presented high concentrations in exposure sites near to heavy traffic avenues (cars, buses, trucks) and may be associated with vehicular sources (Ribeiro *et al.*, 2010).

For Zn (and Co) the highest contents were related to industrial zones and can be associated to the presence of anthropogenic emission sources. The rare earth elements, Fe and Rb probably have soil particles as their main source.

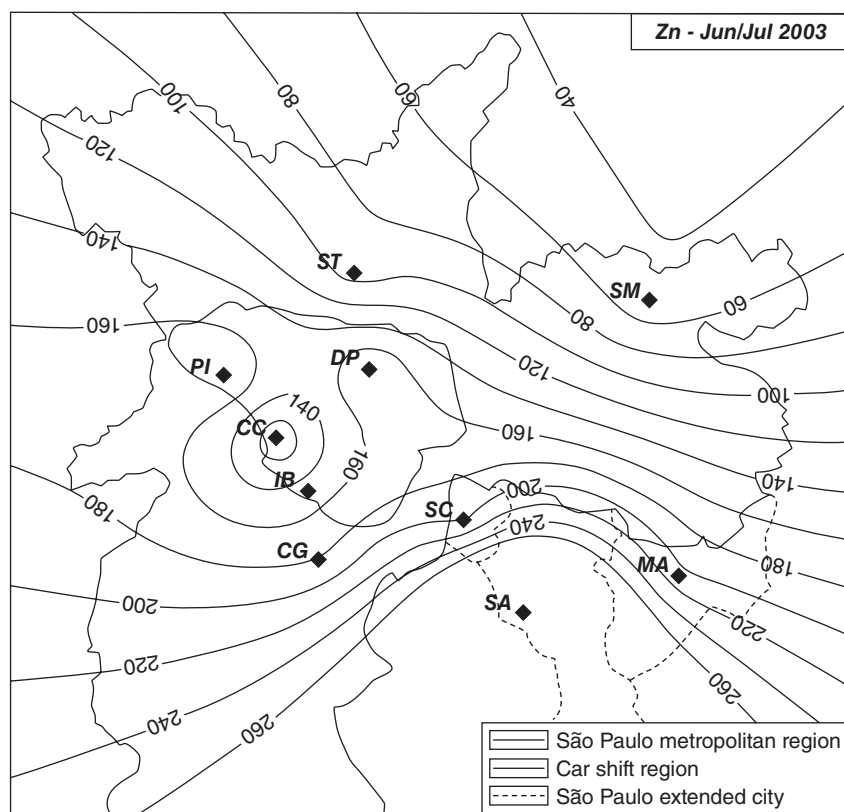


Figure 4.12 Distribution map of Zn in the metropolitan region of São Paulo (June/July 2003). Stations: ST = Santana, IB = Ibirapuera, CG = Congonhas, SA = Santo

André, SC = São Caetano, MA = Maua, CC = Cerqueira Cesar, PI = Pinheiros, DP = Parque D. Pedro, SM = São Miguel (Figueiredo *et al.*, 2007).

4.1.1.6 Conclusion/Outlook: Construction of a Setup for Preventive Healthcare

With bioindicative methods being used for monitoring release, distribution, effects and control of pollutants an integrative approach toward monitoring on larger spatial scales—as well as including quite diverse sets and sources of information—is suggested (multi marked bioindication concept, MMBC; Figure 4.13), meant to be eventually used for preventive healthcare on the scale of counties. Figure 4.13 represents only one proposal of a complete dynamical environmental monitoring system supported by bioindication to integrate human and ecotoxicological approaches. It can combine its measurements parameters according to the particular system to be monitored or the scientific frame of reference. Therefore it seems to have good chances of being transferred to use for pollution control observation in megacities.

To come closer to a prophylactic healthcare system (independent of megacities, smaller cities, rural areas) we should come to a more integrated understanding on an international, interdisciplinary and intercultural level (Simeonow and Simeonova, 2009). For overcoming existing gaps during the international education of pupils and students and for getting common research projects financially sponsored, the public must be convinced by day to day activities (Markert *et al.*, 2008; Trapp and Rein, 2009; Davies and Stephens, 2010).

4.1.2

CO₂ Reduction

4.1.2.1 The Problem

Whenever carbonaceous substances undergo combustion, the terminal⁵⁾—and stable—product will be carbon dioxide CO₂ regardless whether these reduced C compounds were directly or indirectly biogenic and whether combustion was for energy release (heating, propulsion, making electrical energy) or to dispose of these materials. Besides CO₂, there usually are products of incomplete combustion like CO, PAHs and soot. Whereas CO₂ is not really toxic⁶⁾ [levels > 0.5% in air (>13 times the present ambient concentration) are tolerated for weeks, unlike O₂ or N₂ which produce severe adverse effects at just four times the common partial pressure, or unlike highly toxic trace and ultratrace components in air, like O₃, HCN

- 5) There are many other elements—both metals and non-metals—where combustion of whatever binary hydrides by dioxygen does not afford the highest oxide as a stable product but either the element (N) or lower oxides (Sb, Pd, Cu, U, Ce) as main products.
- 6) At almost 2 g/l, CO₂ is considerably denser than air. If vented or produced close to the soil, in some valley or cave, it thus replaces air in those lower places upward, with man and animals in into such areas facing a high risk of asphyxiation. There may even be chain-reaction effects, when hyenas,

vultures, monitor lizards or jackals spot carcasses in these sites, only to become asphyxiated themselves when approaching the meant-to-be prey. A well-known historical cave site of this kind is *Grotta dei cane* (cave of dogs) near Naples (Italy), where volcanogenic CO₂ pours in via crevasses from the nearby Phlegraean fields close to Mount Vesuvius. The “surface level” of CO₂ in this cave is some 70 cm above the ground; hence (adult) humans can safely visit this cave (unless lying down within) whereas dogs are going to die except for the largest ones.

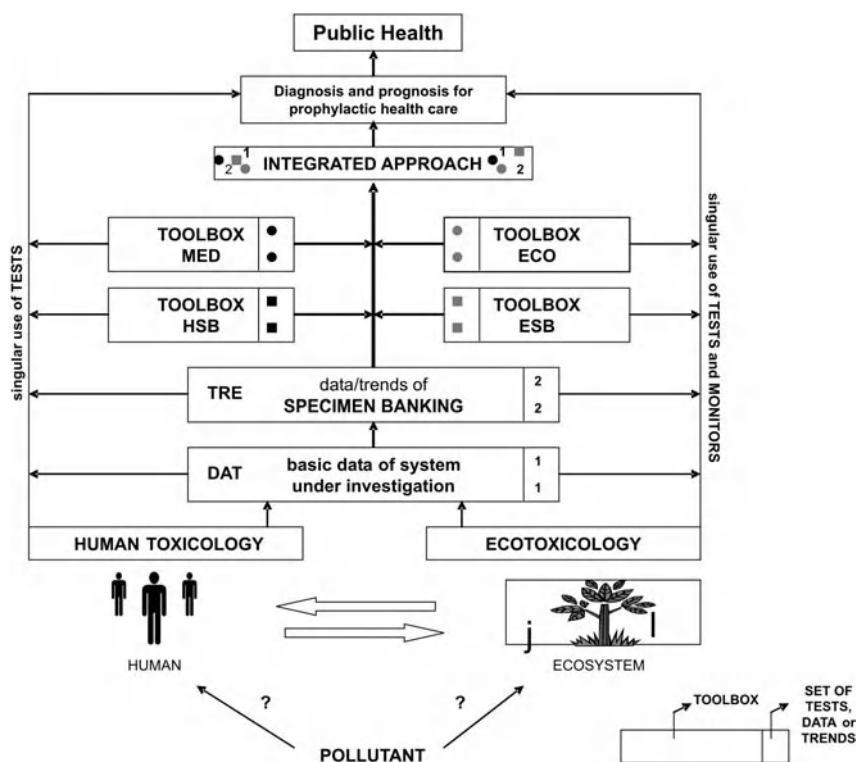


Figure 4.13 Multi-markered bioindication concept (MMBC), an integrative approach on human health care which draws upon a multidisciplinary input organized along several integrated and functional “windows”. MMBC is one way in which bioindicative toolboxes may be organized in a hierarchical framework for the purposes of human and ecotoxicology. In toolboxes MED and ECO, respectively, there are single sets of tests for functional combination in order to obtain an integrated approach toward some specified scientific problem. The toolboxes human specimen banking (HSB) and environmental

specimen banking (ESB) derive from years of research using sample banks for both human and environmental toxicology; thus they can supplement MED and ECO by important information on toxicological and ecotoxicological features of environmental chemicals. This integrated approach is not only to link all the results but to corroborate them with data already available from (eco-)systems research, toxicology, environmental monitoring and specimen banks. Toolboxes TRE and DAT provide parameters required to accomplish this (Markert, Breure and Zechmeister, 2003b).

or NO_2], it is involved in Earth’s atmospheric greenhouse effect at about 50%, its increase since the late eighteenth century thus probably giving rise to substantial changes of global climate.

All hard coal, lignite and crude oil are biogenic fossil⁷⁾ carriers of chemical energy, the paragenesis of which took place excluding air and also without a

7) For methane (natural gas), the biological origins are not quite settled while fissionable uranium (^{235}U) is likewise fossile, left over from before the origin of the solar system while steadily and slowly decaying away by radioactivity ($\approx 1\%$ left over now), but definitely not biogenic.

constant flow of groundwater through the site. Being biogenic, coal, lignite and oil must be expected to contain at least all those elements required to sustain life (i.e., essential elements) in the beginning of paragenesis. Metals such as Mg, Ca, Fe, Zn, Mn (and V, Ni, Ge and others taken up by complexation by porphyrins or sorption to coal) either do not take part in combustion⁸⁾ or form solid oxides to become a fraction of fly-ash, with some of them even isolated from it, like Ge. Particular problems are posed by such elements which form (toxic) volatile oxides during combustion, like As, Zn, Cd or Tl. They must be withheld from the gas stream also. Generally speaking, metal contents of oil are lower than those of coal although there are lipophilic heterocycles like quinolines, pyridines and (benzo-) thiophenes, besides the porphyrins derived from chlorophyll or heme, respectively. Being ligands, all these—making up several percent of certain oils—can keep metals dissolved and “protect” them against adsorption/precipitation to the sediment.

The aim of combustion is to gain energy from it. Most of the energy which can be released is associated with the principal element in fossil fuels, that is, carbon. Essential non-metals N, S and P, parts of them locked up in heterocyclic compounds, are also contained in fossil fuels and their compounds likewise undergo combustion in air. However they do not contribute significantly if at all to the energy released by combustion (note that N oxide formation from either $N_2 + O_2$ or combustion of N-heterocycles is endothermic, i.e., produces less energy than a combustion terminating at N_2). Even so, these compounds (NO_x , SO_2 , HCl) are anhydrides or precursors of strong acids and, moreover, irritants which thus must be kept from getting into air freely. This is done by some washout into solid phases or reduction to reproduce N_2 while CO_2 is produced in much larger (by orders of magnitude) amounts and its formation cannot be avoided if energy production is to be achieved (average contents of C, S, and N in lignite are >90%, some 2% and a few ‰, respectively). Therefore it is difficult or impossible to transfer established methods for cleaning flue gases from N and S oxide impurities to withhold-

8) This statement exactly holds to coal while crude oil paragenesis brings about some unmixing. This is due to metal compounds—except for some chlorides and acetates and a few macrocyclic species—being insoluble in those hydrocarbons which make up crude oil. Hence metals originating from the organisms converting into crude are going to be transferred to the surrounding sediment rather than remaining dissolved in the oil, except for the above and some lipophilic macrocycles: there is a bright red, easy to extract vanadium porphyrin, produced by replacing Mg^{2+} in chlorophyll by VO^{2+} during petrogenesis, which so frequently occurs in crude that it can be considered a typical component and hence

is called Treib's geoporphyrin. In processing crude oils, it is mandatory to extract these and other complexes since their combustion in engines and power plants would give rise to alloys and intermetallic compounds besides volatile oxides which soon would destroy the interfaces of cylinders by corrosion or alloy deposition. Moreover hydrogenation and cracking catalysts (platinum group metals, rhenium, nickel) are sensitive to “poisoning” by many of them.

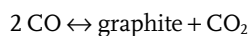
As a bonus, certain elements “suiting” the cavity size of porphyrins and/or producing lipophilic chlorides are best obtained from this purification step, including indium and germanium besides V.

ing CO₂ or putting it into some state or site where it will not affect radiative forcing in the troposphere and thus change climate. Rather, CO₂ must be sequestered and then deposited in either solid (dry ice or gas hydrate, respectively), liquefied or gaseous states in secluded sites (no exchange with the atmosphere within an foreseeable future of centuries at least) or be transformed into some agreeable speciation form other than CO₂ by chemical energy sources independent of direct reduction. Quite similarly, SO₂ may be sequestered and processed further as such or be converted into gypsum.

Full-scale [up to C(IV)] carbon oxidation cannot be avoided as it releases most of the chemical energy only, and incomplete oxidation provides strongly poisonous and/or carcinogenic products (see above), like CO, PAHs and soot. Taking graphite⁹⁾ to actually represent coal, the corresponding standard free energies of formation are:

Graphite:	0 kJ/mol (<i>by definition</i>)
CO:	-137.15 kJ/mol
CO ₂ :	-394.37 kJ/mol

Accordingly, when carbon (coal ≈ graphite) is combusted into CO (rather than CO₂), for example, by high-temperature reactions with water vapor (syngas reaction) or various metal oxides, just about 35% of that amount of energy are released which can be obtained by C oxidation using O₂, therefore Boudouard's equilibrium:



is far to the right side under common conditions. Likewise, PAHs and similar intermediates of CO combustion are energy-rich, often even endothermic¹⁰⁾ compounds. With the latter oxidation intermediates also being highly toxic, full

9) In normal conditions, the stable form of carbon is graphite [neither diamond nor fullerenes C₆₀, C₇₀, C₇₈, and so on although both are metastable (kinetically inert) to behave as either "a girl's best friend" or a special semiconductor, high-hardness tool component, or an interesting component of organic solar cells (fullerenes), or superconductors], hence $\Delta G_{\text{graphite}; 298\text{K}} = 0 \text{ kJ/mol by definition}$. In addition graphite (soot particles) are the final products of PAHs linked to each other in one plane by oxidative dehydrogenation. Thus, intermediate structures are similar to those seen in crude oil paragenesis and thermal processing (PAHs from coal tar!).

10) Benzene, toluene, naphthalene, biphenyl and all the other aromatics and PAHs without heteroatoms are thermodynamically unstable toward both decay into the elements C and H and—of

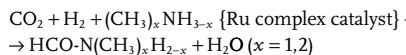
course, as methane is an exothermic compound—into C and CH₄. Hence their combustion is going to produce far more heat than that of coal (≈graphite) itself. In fact, benzene additions to car fuel (up to 35%!) were used to control pathways of intra-engine combustion in earlier (pre-WW II) days as an anti-knock agent. However, benzene, naphthalene, and PAH combustions are going to produce lots of soot. Perhaps these soot particles, as catalytic interfaces, are even involved in the effect, favoring adsorption and controlled recombination of radicals present in the gas phase above the moving piston, radicals which would else unleash explosive chain reactions ("knocking"). See Porter (1967) for details, concerning a similar case, namely intra-engine products of lead tetraalkyl chemistry.

oxidation of CO into CO₂ is both an environmental requirement and some of efficient energy conversion. Hence we must cope with CO₂ and its specific diverse secondary effects on the environment, which include both acidification of waters, dissolution of carbonate minerals [including biogenic ones like corals (calcite) and clam, snail shells (aragonite)] and its property to absorb IR radiation (greenhouse effect). Unless CO₂ is going to be deposited in carbonates (which would require an ample source of alkaline oxides) or in its native form, the law of conservation of energy requires the energy for “reversion” of C oxidation upon inclusion into organic compounds¹¹⁾ to be taken from some other than thermochemical source, for example, a photoreaction. This source of energy must be independent from thermochemistry.

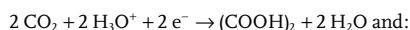
Possible (theoretical) options which fulfill this criterion include solar energy, energy forms derived from it (wind, flowing water other than tidal energy but including ocean currents) and nuclear energy. However, the energies required to introduce CO₂ (back) into organic molecules are quite substantial, with large overvoltages observed in, for example, electrochemical production of oxalic acid; in addition, efficiencies of producing electrical energy from such sources are (necessarily) <<100%, so it would be a fancy to run fossil fuel power plants and others side by side just to “treat” the CO₂ emitted by the former by some method of reduction; rather there should be direct substitution of fossil energy carriers by “alternative” sources.

Nevertheless the amount of CO₂ already released causes quite a number of problems, calling for appropriate action, and there is a large-scale blueprint in living nature for photochemical reduction of CO₂ which recently was also mimicked by semiconductor-mediated photoelectrochemistry and some photoreactions of Ru and Re complexes (Walther, Ruben, and Rau, 1999), namely photosynthesis. Like in photosynthesis by photobacteria,¹²⁾ all these processes use electron sources for CO₂ reduction which are more accessible than water, often sulfur compounds like sulfite SO₃²⁻, which would also be afforded by cleaning flue gases. Demonstrated examples include photoreductions of CO₂ at TiO₂ (mixed with copper grains which direct electrons and increase product selectivity into CH₄), ZnSe, InP, or CdS. The latter photoreaction works in visible light (CdS is bright-orange to yellow) and produces carboxylic acids and amino acids, if NH₄⁺ or nitrate are added to the mixture. In these photoreactions electrons from SO₃²⁻ are consumed

- 11) By now (2011), there are few examples of chemical reactions using CO₂ in technical dimensions, including the production of formamide solvents:



or of oxalates, oxalic acid:

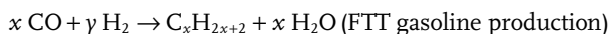
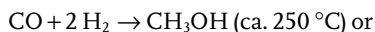
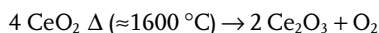
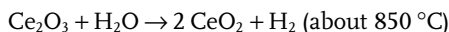


In either case, electrical energy from various sources is needed for production of precursors sodium metal, H₂.

- 12) In photobacteria, H₂S (Photothiorhodaceae) or Fe(II) or (some photoassisted heterotrophic organisms) even dissolved organic matter are used as electron sources for CO₂ reduction.

by holes (producing sulfate or dithionate¹³⁾) while conduction band electrons are bound to CO₂ carbon atoms.

Both photosynthesis (plantations which bind CO₂ into wood or other kinds of biomass) and photoelectrochemical methods thus meet the criterion to remove CO₂ by some reduction pathway which is completely independent of fossil fuels. Likewise CO₂ and water can be co-reduced in a solar-thermal manner eventually to produce methanol CH₃OH or hydrocarbon fuels by Fischer–Tropsch type syngas conversion after thermolysis at cerium (rare earth element) oxide interfaces exposed to concentrated sunlight [solar oven,¹⁴⁾ concentration factor (CF) > 2000] to heat it above 1500 °C (Smith, 2009):



In the latter system, recently devised in Switzerland, and in methane combustion after processing CO₂ photoreduced at TiO₂/Cu there is the chance to close the carbon cycle without changing too much at present technologies of energy conversion and traffic propulsion, like it is with “biofuels” plant oil or ethanol from CO₂-sequestering plantations. While CO₂ could be kept from piling up in the atmosphere for longer periods of time, one must also address aspects of efficiency in devoting pretty large areas to either kind of measure (bear in mind that only direct sunlight, unscattered by any clouds, can be focused by a mirror device): taking all his/her industrial and private activities, for example, the average German now consumes 800 W of electrical energy, and there are some 230 of them per km² (figures for other highly developed countries are similar), corresponding to 184 kW/km², or >400 kW/km² (mW/m²) given the limited efficiency of power plants thereafter. At first glance, this compares comfortably well to the Central European solar energy impact of some 1150 kWh/m² per year (with a maximum

13) Unless for such a “sacrificial donor” which yields electrons to valence band holes (which can be more oxidizing than even fluorine), including water, other solvents or organic pollutants thus to be removed the holes would attack the very anion partial lattice of the semiconductor, rapidly (often within minutes in sunlight) corroding it.

14) The maximum temperature which can be reached in a solar oven corresponds to that of the very solar photosphere owing to blackbody conversion of the original solar spectrum, that is, some 5650 °C. The

practical limits are some 3600 °C in solar ovens of CF ≈ 20 000 at Albuquerque (New Mexico, USA) and a small one at Cologne while the two huge (MW thermal power) and thus famous devices at Odeillo (French Pyrenees) and Parkent (Uzbekistan) do not provide that exact a focus, limiting temperatures to somewhat beyond 3000 °C, even though the French one was the first apparatus in which fusing tantalum (melting point = 2996 °C) sponge into bulk metal was accomplished (electrical arcs would rather convert it into carbide TaC and nitride TaN).

in the Pannonian plate, Austria and Western Hungary) or an annual average of some 130 W/m^2 . Alas, photosynthesis is a poor process: unless doing intense fertilization (with fertilizers which are produced employing copious amounts of fossil energy carriers for hydrogen production) on certain crops (e.g., corn monocultures may yield some 3–4%, with common efficiencies of <1%, that is, $<1.3 \text{ W/m}^2$ —just three times what is needed when covering Germany’s entire area by “energy plantations”). Polycrystalline solar cells coupled to H_2 production by electrolysis perform much better, at a total yield of some 9% (12 W/m^2 annual average) while the efficiency of photoelectrochemical CO_2 reduction is about 1–2%, a little superior to photosynthesis (this is because, e.g., the titania-based system can make use of UV quanta only). Photosynthetic varieties of plankton algae or cyanobacteria (cultures sometimes supplied by flue gas directly to consume all C, N and S from it), with the latter producing substantial elemental H_2 , do not surpass 1% by much, let alone the fact that never significant fuel/dihydrogen amounts have been produced by this method.

Although commonly being rather a trace component of the atmosphere, and being too rare to provide optimal efficiency of photosynthesis, the increase in output obtained when increasing the CO_2 partial pressure is less than proportional to the former. Hence the biota cannot directly counter-act a fast increase in atmospheric CO_2 —be it anthropogenic, or caused by volcanoes, changing geochemistry or erosion rates—completely, which actually is obvious from the seasonal fine-structure of Keeling’s CO_2 curve (Figure 4.14).

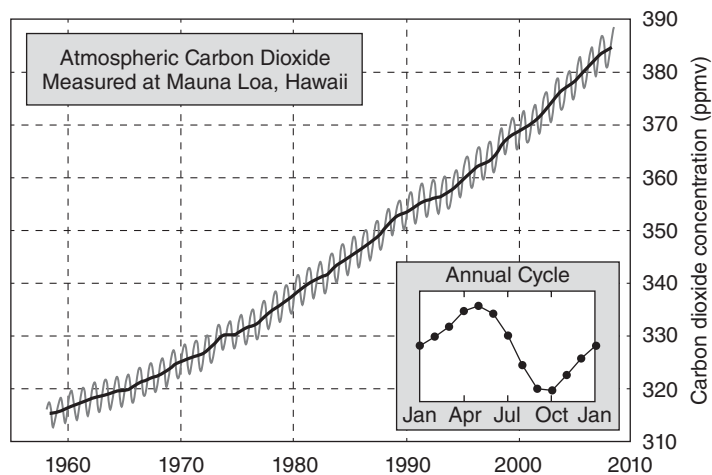


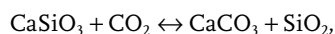
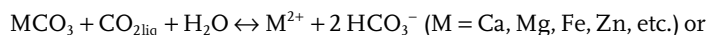
Figure 4.14 The development of atmospheric CO_2 levels between 1957 and the early twenty-first century at Mauna Loa summit site (Hawaii, USA). Note the annual variation in an interplay of enhanced production (wintertime heating) and consumption (photosynthesis during summer) which,

however, can cancel only some part of the corresponding emissions (about 70%). The gray curve shows the average monthly concentrations, and the black curve is a moving 12 month average (Hawaiian Volcano Observatory, April 2008).

Both the production (by human population and her economic activities) and consumption (by photosynthesis) of CO_2 are strongly biased geographically, most of both activities taking place in the Northern hemisphere (photosynthesis in oceans and agrarian regions, human activities mainly along the shores of Europe, Asia and northern America). Some 70–80% of the ΔCO_2 (≈ 5 ppm in northern winter-times, i.e., 1.4% of total inventory) are re-claimed by biota during northern spring- and summertimes. The (1997) Kyoto Protocol takes this geographical imbalance into account by allowing the “nomination” of (re-)forestation activities as a compensation for CO_2 emissions in emission certificate trading.

This is just another argument for replacing fossil energy sources for providing both electricity and heat by solar and solar-derived sources rather than trying to “capture” CO_2 by such energy sources, even though photosynthesis does part of this job (see below). As a by-effect, fossil resources would remain available for more sophisticated uses than energy production for many decades but there is some time to go until this is fully accomplished, even and especially when nuclear energy is less and less accepted in the aftermath of Fukushima events. Hence one must consider for now how to use fossil energy carriers without “leaking” CO_2 to the free atmosphere.

Of course, such a deposition method of CO_2 must be sufficiently effective and use appropriate spaces in terms of “burying” billions of tonnes/year of CO_2 for decades to come and must be safe in the inclusion of this asphyxiating gas. When relocating CO_2 after some combustion process into the cavity or porous sediment from which the fossil fuel was taken before, there are issues (besides tightness; which can rarely be taken for granted, mainly with abandoned natural gas reservoirs) whether: (i) the capacity is sufficient (the molar volume of liquid CO_2 is about 40 cm^3 , as compared to some 15 cm^3 per carbon in crude oil) and (ii) is the enclosure sufficiently stable: will there be any attack on carbonate or silicate minerals under high pressure according to:



both causing breakdown, crack formation or pitting corrosion of bedrock?

With the temperature increasing when getting deeper in sediment, both liquid or supercritical carbon dioxide [critical temperature (T_c) = 31°C , critical pressure (p_c) = 74 bar] and its hydrate $8\text{CO}_2 \cdot 46\text{H}_2\text{O}$ produce substantial pressures to be compensated by at least hundreds of meters of overlaying sediment or water column. Hence outbreaks are likely but must be avoided as CO_2 is toxic. Things [the carbon capture and storage (CCS) approach] would likely run out of control if local heating could contribute to this pressure or carbonates might undergo pitting corrosion like in formation of caves (Figure 4.15). Accordingly, underground CO_2 deposition must not be undertaken where geothermal heating—let alone volcano activities—must be anticipated. Even though former natural gas deposits in salt diapirs withheld gas pressures of hundreds of bars and some diapirs are used for storing natural gas (methane) secondarily at similar pressures,

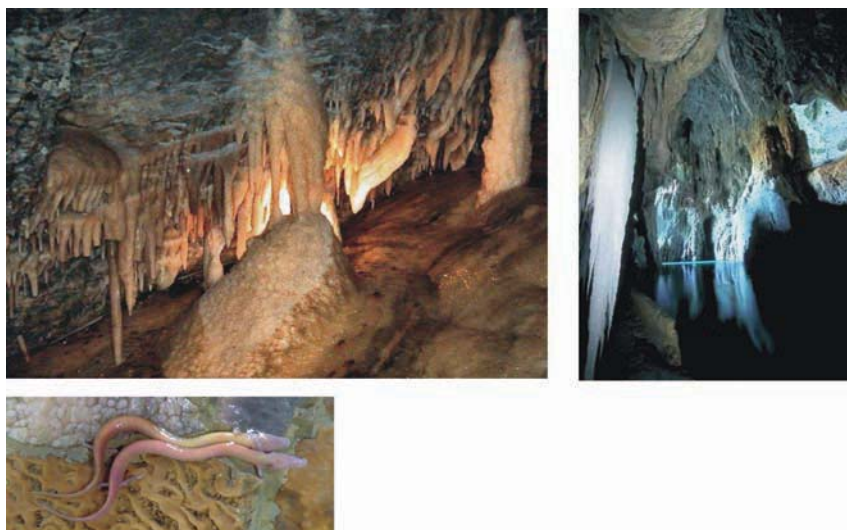


Figure 4.15 Hanging stones in caves (upper photos). Like shown in the above equation (for $M = \text{Ca}$), calcite or aragonite are attacked by dissolved CO_2 , forming hydrogencarbonate (bicarbonate) which is soluble in water. If the temperature rises or the CO_2 partial pressure is reduced, the reaction is reversed to re-precipitate MCO_3 , often including other metals such as Mg or Fe (dolomite, siderocalcite). Thus, attempts to dispose of pressure-liquified CO_2 in calcareous

formations would be most dangerous as it would make its way out as soon as there are (even catalytic amounts of) water, making holes and crevasses to escape. Lower photo: Two olms (*Proteus anguinus*) in the Postojna Cave, Slovenia. Olms are blind amphibians endemic to the subterranean waters of caves. They are adapted to the darkness. Upper photographs courtesy of: www.showcaves.com. Lower photo courtesy of: wikipedia, Bostjan Burger.

diapirs are not considered safe deposits for CO_2 . Gas hydrate formation in deep salty aquifers or the open ocean tends to cause problems too: deep landborne aquifers are rather hot, with $8\text{CO}_2 + 46\text{H}_2\text{O}$ breaking down above some 15°C regardless of the pressure while the ocean is alkaline, eventually re-dissolving the gas hydrate by forming HCO_3^- and corresponding acidification.¹⁵⁾

Given this, CCS projects mostly point at either very deep saline aquifers, coal beds¹⁶⁾ or exploited gas or oil deposits. One such site located offshore (between

15) The only natural subaquatic liquid $\text{CO}_2 + \text{CO}_2$ hydrate “pond” which was discovered so far [1400m below, near Yonaguni Island between Japan (Ryukyu Archipelago), Taiwan and PR China], formed and replenished by CO_2 venting from submarine fumaroles in a valley, is rather stable only because it is covered by several decimeters of muddy sediment separating it from the open ocean water.

Nevertheless, acidification-based toxicity around this site is evident: biodiversity among bacteria is considerably reduced as compared to nearby sites although certain anaerobic ones employ liquid CO_2 both as oxidant and (being lithoautotrophic) as a carbon source while clams are absent and mobile fishes, starfish and cephalopods apparently avoid the place (Inagaki *et al.*, 2005; Caldeira *et al.*, 2009).

Norway and Scotland) and long since been used for corresponding experiments (it still is an experiment rather than an established method) is the Sleipner gas field. Abandoned (exploited) natural gas cavities are suited for re-filling by combustion product CO_2 but mostly are far remote from the main consumer sites, for example, in Siberia, Turkmenistan or the Middle East (Qatar, Iran).

4.1.2.2 Applicable Principles and Technical Solutions

Which kinds of chemical or pseudochemical reactions can be used in order to withhold carbon dioxide? The possible options include:

- 1) Gas hydrate formation [deposition in either deep ocean or (exceptionally cold) saline aquifers];
- 2) Reactions between CO_2 and alkaline reactants (silicates, oxides) to yield carbonates, alternative alkaline reactants being;
- 3) Organic bases such as monoethanol amine, absorption to be followed by thermic release and subsequent deposition of CO_2 ; ¹⁷⁾
- 4) Adsorption onto hard coal (ambient coal beds);
- 5) Reduction of CO_2 by either chemical, thermochemical (cf. the above cerium-based cycle) or photochemical methods, including;
- 6) Photosynthesis accomplished by either “higher” green plants, algae or bacteria. Besides all this;
- 7) Carbon may be decoupled from combustion matter flows altogether by doing coal gasification and syngas conversion (IGCC technology, see below) before the H_2 left over is passed into either gas turbine power plants or fuel cells, facilitating the extraction and eventual deposition of CO_2 from the stream, which generally is;
- 8) Done as a liquid or supercritical fluid ($T > 31^\circ\text{C}$) in various kinds of porous sediments like “empty” gas or crude oil deposits.

The latter options (7, 8) are that ones which are most pursued these days.

Concerning (1): gas hydrates are formed by water (and likewise by solvents having similar internal structures) molecules constructing a kind of spider’s web

- 16) From an economic point of view, it is totally pointless to try to dig out hard coal from sites, say, 2000 m below the soil surface in developed countries. Nevertheless, lots of coal are located in such depths, for example, in Western Poland, adsorbing any unpolar gas which is around. To coal miners, this is a constant hazard, with adsorbed CH_4 , CO , or H_2S being replaced by N_2 and O_2 once a mine is created, causing risks of either

explosion or poisoning. CO_2 can likewise be adsorbed, replacing methane from coal to get natural gas as a by-product, however. This exchange does not require the presence of humans at the coal beds but making some cracks then open for gas adsorption far underground would do. The same method and reagent is sometimes used to clear flue gases of SO_2 also.

17)

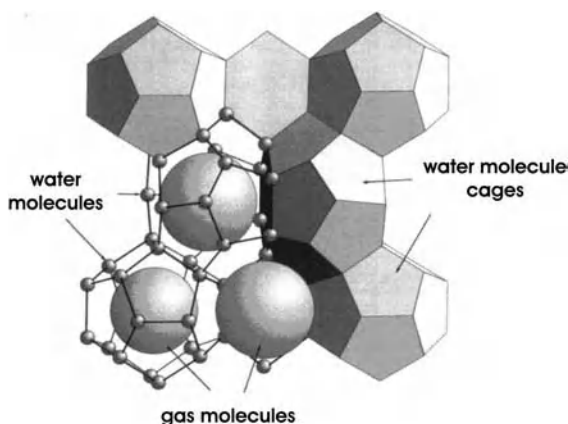


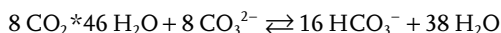
Figure 4.16 Structure of a typical clathrate hydrate. The network of hydrogen bridges among water molecules rearranges upon cavity formation in a hydrate to form some pentagon dodecahedron. Photograph courtesy of: www.gashydrat.de.

around (noble gas, mercury) atoms or small molecules (Figure 4.16), with the melting point of this hydrate slightly in excess of pure water (+0.01 °C).

As these hydrates melt higher than water itself, passing atoms or molecules like CO₂, krypton, CHCl₃, or Br₂ into cold liquid water (say, +5 °C) will cause solids to form and precipitate. Besides the heavy noble¹⁸⁾ gases Ar, Kr and Xe, compounds which are most ready to produce gas hydrates include. CO₂, Cl₂, Br₂, CH₄, heavier alkanes (e.g., propane hydrate often blocking gas flow in pipelines if natural gas is not properly dried) and CHCl₃. Methane hydrate which occurs in deeper ocean layers can be used as an energy resource (which local bacteria also do). The density of water ice (ice I¹⁹⁾) is some 9% smaller than that of cold water, making ice float on water, because hydrogen bonds construct a crystal networks which already contain voids among the water molecules rather than their being densely packed. Upon solvation of the above species, H bonds rearrange in space to create yet larger voids and accommodate the included species. In the deep ocean ($T \approx +2\text{ °C}$), the pressure required to maintain this combined (mixed-crystal) structure is some 35 bar for both CO₂ and CH₄, increasing to >200 bar at 15 °C. Thus, when passing liquid CO₂ [which itself only exists at pressures above 5.6 bar (triple point)] into sea water, the hydrate will form below 350 m depth. However, CO₂ hydrate will not persist in sea water as an alkaline buffer solution (pH = 8.3) which converts CO₂ hydrate lumps into bicarbonate:

- 18) Kr and Xe are fairly rare but argon, although it cannot be made to undergo chemical reaction (hence is really "noble") is the most common atmospheric gas other than N₂, O₂ and water vapor!
- 19) Ice I is the kind of water ice stable under ambient pressure and up to a few kbars. High pressure modifications of solid

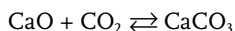
water—up to ice XIV at least—do behave like common solids as they are more dense than melting liquid water in the same pressure, temperature conditions. So this famous anomaly of water is restricted to low pressures while in satellites of outer planets molten-water oceans lie *above* highly compressed water ice.



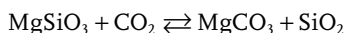
In the surroundings marine animals—which are adapted to very precisely constant pH except for estuary-dwellers or anadromic fishes—are going to be compromised or even killed by the pH reduction. Given the lability and lack of nutrient sources in the deepest ocean (hadal²⁰), the local ecosystems will respond even worse to deposition of CO_2 in marine trenches like Mariana or Cayman trenches which also was considered for the reduced risk of upward mixing. However, at pressures >70 bar hydrate formation from the supercritical fluid no longer occurs readily.

For all these reasons, ecological consequences would be even more serious than manganese nodule mining. In fresh waters, the CO_2 hydrate would be stable if water is slightly acidic,²¹ but there are very few large, sufficiently deep lakes all over Europe, essentially three: Lago Maggiore (Italy), Lake Como (Italy/Switzerland) and Tinnsjøen (Norway).

Concerning (2): many metal oxides can absorb and bind CO_2 for their being basic, for example, CaO used for this purpose in closed-circuit (rebreather) diving apparatuses:



However, these oxides are usually manufactured by heating the corresponding carbonates, thus releasing exactly as much CO_2 as can be fixed afterwards. Until now, this heating in addition is accomplished by burning fossil fuels, so much that CaO production for making cement and concretes contributes several percent of total anthropogenic CO_2 inputs. A possible and probably useful exception from this rule is the reaction between CO_2 and natural Mg silicates analogous to the Urey equilibrium (for which $M = \text{Ca}$ rather than Mg, putting wollastonite CaSiO_3 , calcite and amorphous silica into equilibrium) which latter controls the dynamics (and viscosity) of CO_2 and silicate melts during volcanic eruptions:



20) Hadal: the deepest parts of the oceans, that is, the ocean trenches between 5 and 11 km of depth. The deep basins into which the trenches cut, the abyss, are shallower and called “abyssal”.

21) The big and sufficiently deep (Lake Victoria >1100 m; Lake Malawi = some 700 m) East African lakes are strongly alkaline (much more so than seawater, pH >>9) which would spell rapid dissolution of CO_2 hydrate. Lake Baikal (the biggest and deepest freshwater basin in the world) and nearby (northern Mongolia) Hovs Gol are slightly acidic, likewise sufficiently deep (>>350 m) rift valley basins. The latter fact—which they share with the above big lakes of the East African Rift Valley

extending from Israel [Lake Tiberias (Sea of Galilee)] and Palestine (Jordan valley) all the way down to Malawi and Mocambique—however is not just the basis for their being so deep but also implies that tremendous geothermal energy may be unleashed at any time under such a deposit of CO_2 hydrates. If so, clathrate hydrates will rapidly give away CO_2 which in such amounts cannot either be retained by dissolution, causing a catastrophic eruption of CO_2 gas like that which occurred near Lake Nyos volcano (Cameroon) in 1986, killing some 1700 humans and tens of thousands of cattle when the CO_2 ran down the densely occupied volcano slopes.

Unlike hydroxides and oxides of alkali and heavier alkaline earth metals, these Mg silicates can be obtained by mining rather than produced by incineration requiring additional energy.

Concerning (3): moist (water-containing) ethanol amine (2-hydroxyethyl amine²²⁾) will react with CO₂ to yield insoluble 2-(hydroxyethyl)-ammonium hydrogencarbonate. After isolation it is thermolyzed, allowing for subsequent deposition of CO₂, while ethanol amine is recycled into the cleaning gear. It just needs to be partially dehydrated on a regular schedule for maintaining its activity as a transportation agent.

Concerning (4): both lignite and hard (black) coal are distinguished by complicated inner structures, pores and accordingly sorbent properties which come close to those of activated carbon sorbents. Activated coke is produced simply by thermal desorption of previous sorbates from coal by heating it up to the point where sorption sites are set free. Directly after mining, moist coal uses to keep gases adsorbed which, like CO and CH₄, can pose substantial risks to coal miners when desorption/sorbate exchange take place already right in the mine.

New sorbates, including the main components of air, are brought into contact with coal now, causing the former sorbate inventory to release and penetrate into the mine cavities, including gases like CH₄, CO, H₂S which are both explosive when mixed with air and capable of incapacitating and killing miners as poisons also. It is no more meaningful economically to mine deep coal beds in, for example, the European Union or northern America, but such coal beds are potential sorbent sites for deposition of CO₂. With CO₂ being more tightly adsorbed than the above gases, natural gas can be produced from such coal beds also, besides of CO₂ sequestration.

Concerning (5): there are novel developments on CO₂ solar-thermal splitting, mostly by cerium compounds as mediators (see above) to store solar energy consuming CO₂ in liquid fuels, which now get beyond mere demonstration plants. As an industrial raw material, CO₂ actually got some significance already, with the corresponding reactions for production of solvent dimethyl formamide (DMF), oxalates and alkali formates (from hydrides and CO₂) discussed above. Reactions with hot Mg or molten alkali metals yield oxalates.

Likewise already mentioned are those large-scale electrochemical procedures which afford—depending on the kind (material) of the cathode and solvent (water or organic) oxalate C₂O₄²⁻, glyoxylate HCO—COO⁻, methane or methanol while reductive coupling to alkenes yields C_{3+x} carboxylic acids. Yet, we are generally left with the problem that much more²³⁾ primary energy is required to induce these transformation than was released by making the very CO₂ by combustion which is going to be removed by these coupling or reduction processes. Once again, any meaningful process must make use of hydrogen or electrons from non-fossil sources (photovoltaic devices linked to electrolysis, etc.). Besides, just a few million

22) Colorless, viscous, hydrophilic liquid (mp = 10.5 °C, bp = 171 °C) which, however, cannot be mixed with diethyl ether or aliphatic hydrocarbons.

23) The main reason among the electrochemical processes are the large overvoltages (electrochemical equivalents

of activation barriers) which must be overcome to induce these reductions even on suitable, for example, lead, indium, or copper electrodes. Before, the electrical energy to be used was produced and converted into direct current with an overall efficiency of 45% at best.

tonnes of these chemical commodities are consumed per year worldwide whereas some 7 bio. t of CO_2 are released (even excluding slash-and-burn agriculture and deforestation), implying just a minute fraction of CO_2 can be funneled into group (5) pathways. The same holds for polymer production which, producing single-use items such as transportation bags mainly, often also is suggested that it should be based on CO_2 consumption: even though global use of plastics has skyrocketed to some 250 mio t/year recently, this is (fortunately!) short of the other pathways by almost two orders of magnitude. Accordingly, the focus must be placed to both deposition of CO_2 and/or dealing with it by photosynthesis, that is, methods (4), (8) and (6). Alas, plants respond to more CO_2 too weakly (Figure 4.17). Thus a complete tackling with additional CO_2 will succeed in isolated greenhouse-like systems rather than the free atmosphere only.

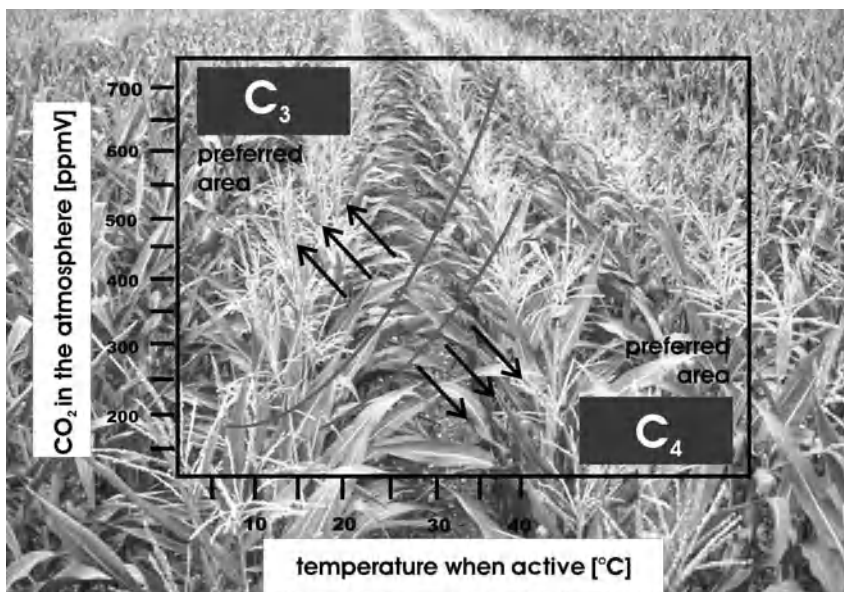
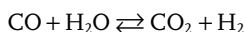
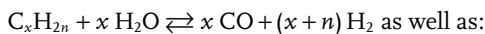
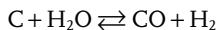


Figure 4.17 The C_3 and C_4 plants which use different phosphorylated intermediates for binding CO_2 respond to changing CO_2 atmospheric levels in different ways concerning both partial pressure and temperature. Those plants in Arctic regions (mosses, grasses) which are C_3 plants and most exposed to recent global change will not yet really respond to more CO_2 except in the few “hottest” summer weeks, unless CO_2 levels far beyond 400 ppm are reached. Hence they are not yet in a position to respond to more CO_2 by increased photosynthesis unless the situation gets even worse than now (in addition, large venting of greenhouse gas CH_4 from arctic swamps and wetlands can be

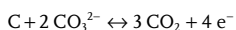
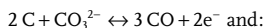
anticipated). C_4 plants like corn can achieve (relatively) very efficient photosynthesis at the present and even far lower CO_2 levels (down to <10 ppm!), with a bonus performance at tropical temperatures only. So the area where (appropriate) plantations will actually cope with additional CO_2 in the atmosphere, is fairly contrived. This effect must be taken into account when considering CO_2 counter-acting by plants, given there is any chance to select either C_3 or C_4 plants of corresponding performance for being grown on a large scale in given temperature and CO_2 level regimes (Ehleringer and Cerling, 2001). Background photograph: Syngenta; scheme overlaid by the authors.

Concerning (7): coal will react with hot ($\approx 1000^\circ\text{C}$) water vapor to produce CO and dihydrogen (syngas reaction, coal gasification). At lower temperatures, CO will also abstract oxygen from water eventually converting coal fuels into pure H_2 easily to be separated from CO_2 by-product and to be used, for example, in fuel cells [integrated gasification combined cycle (IGCC) technology]:



The “combination” of this combined cycle refers to the two-step procedure, with first combusting a gas or vapor fuel (mainly H_2) to be burned in a gas turbine quite similar to the jet engine of an airplane²⁴⁾ by-producing very hot water vapor. This steam is used to make more steam (by water injection) which then propels a steam turbine like in a classical fossil or boiling-water nuclear power-plant. This twin-stage process will increase the overall electrical efficiency up to almost 60%. The combustible gas can be produced by reacting quite diverse C-containing fuels with H_2O vapor at about 1000°C , not needing to take coal but also consuming crude oil, lignite, oil shales, recent plant materials (renewable resources) such as plant oils, wood, wood scrap, peat, straw and so on. Sufficiently hot water vapor is obtained from the primary process whereas CO_2 is put aside before even entering a combustion site, allowing for easier discarding or use. There is historical precedent: Coal gasification was already being tried for fuel cell use in the nineteenth century²⁵⁾ while, beginning in the 1920s, it was a precondition for using lignite for liquid fuel production, making CO and gasoline from CO/H_2 mixtures over heterogeneous catalysts. By the end of World War II, it was even tried to

- 24) The uncoupling of mechanical energy from the burning gas jet is done quite in the manner of “turboprop” devices in aircraft or turbines propelling helicopters, here, propelling a generator rather than turning round a crank or rotor.
- 25) Besides running “conventional” hydrogen fuel cells, it was also attempted to run the following C-based redox system at appropriate electrodes in carbonate melts (Ostwald):



in alkali carbonate melts. Although these oxidations might be mediated by platinum group metal electrodes, these are rapidly degraded in such conditions (even Ru or Ir); and accordingly no appropriate electrode material then was at hand. Now Zr or Ta alloys or some semiconductor ceramics would withstand such operating

conditions but another way of electrooxidizing coal was identified recently: attack by mercury(II) compounds or bis-pyrimidine-platinum complexes in hot H_2SO_4 solutions (Periana *et al.*, 1993, 1998) where CH_4 and larger hydrocarbons and coal undergo CH activation to give CH_3OH and higher alcohols, with H_2SO_4 being the eventual oxidant at some 200°C . For processes not to be preceded by coal gasification, various ways of partially or almost totally dissolving coal by cleavage of ether, ester and diaryl oxide moieties can be used, leaving the remains open for electrochemical degradation, at least at Ru interfaces. Suitable solvents include tetraline (Hooper and Evans, 1980), a saturated solution of zinc chloride in methanol (Shinn and Vermeulen, 1980) and dimethyl formamide (authors’ own observations).

integrate coal gasification devices into jet airplanes when crude oil and jet fuel were no longer available. Now modern high-T fuel cells also give proof that IGCC can be run in small, de-centralized energy conversion units.

CO₂ is then liquified by cooling and applying pressure to put (pump) it to a disposal site. Now we must consider the products and by-effects of these various (potential) methods to get rid of combustion-related CO₂.

Processes (1), (3) and (7) produce no by-products but are reversible processes which bear the risk that CO₂ withholding fails when heat gets into the disposal plant. Processes (2), (5) and (6) each bring about typical reaction products, with plants (case/method 6) later possibly being used as food, fodder, or a source of wood and other materials. Both (4) and (8) can provide natural gas as a by-product. Process (5) yields solid organic acids or certain solvents (methanol, DMF).

A device withholding or actively absorbing CO₂ can be constructed in quite different manners, the most simple case being an extensive plantation.

4.1.2.3 A Practical Example

The main option pursued in studies and pilot plants (Figure 4.18 and additions) now is deposition of CO₂ outside of atmosphere and biosphere (the latter statement both disregarding those chemolithoautotrophs dwelling in deep sediment and bedrock layers and possibly using CO₂ as well as excluding deep-ocean deposition), uncoupling the gas from geo- or geobiochemical cycles which include the atmosphere: if CO₂ returned to the atmosphere sooner or later, at once or in centuries to come, it would once again contribute to both greenhouse effect and ocean acidification. Two options are to be analyzed more deeply:

- 1) Deep-ocean deposition;
- 2) Pumping CO₂ into abandoned oil and gas reservoirs.

Until now, deposition is done in cavities below sea ground which were created or, rather, "emptied," during oil and gas production below the North or Caspian Seas. Sometimes this is already part of the common procedure as natural gas, much like "biogas", often contains substantial CO₂ which is separated and sometimes directly re-pumped into the mining site. In addition, in mixed oil-gas mining supercritical CO₂ is employed as a nonpolar "solvent" replacing tensides in washing out the major part of oil from the sediment (otherwise, little more than 25% of the actual stock could be mined). If natural gas remained in the upper parts of the "dome" at often many MPa pressure, it can be considered gas-tight also if the (former) fossil fuel repository is now converted from an (indirect) source into a sink for CO₂. However the combustion of hydrocarbons means an extension of the molar volume, and thus the gas stock volume over an oil layer is also required to accommodate all the CO₂ produced from the contents of this site. However, certain sites on solid land can also be used.

Problems with the former method were discussed above but the latter was actually tried in pilot experiments, first in Canada and Poland and now also in Germany (Ketzin, *Land* of Brandenburg). However, actually passing the products of a coal or lignite power plant (lignite is mined and used locally in Lower Lusatia) into

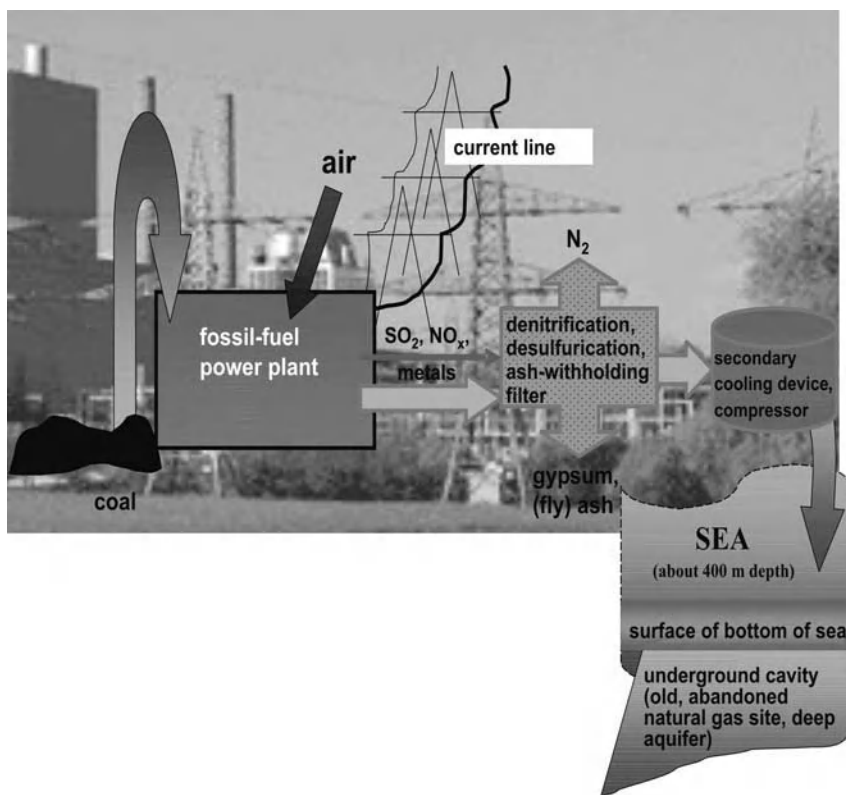


Figure 4.18 A flow diagram linking coal mining and combustion, via classical flue gas treatment to remove all NO_x , SO_2 and metalliferous dust, to CO_2 sequestration. First, the remaining gas must be cooled below 31°C [T_c (critical temperature) of CO_2] in order to

liquefy it. Prior fractionation is required to remove the more corrosive and also redox-active non-metal oxides NO_x and SO_2 for protection of the deposition site. Background-photograph: Windandler; scheme overlaid by the authors.

underground deposition sites is still one step (at least) in the future, let alone that the CO_2 amounts²⁶⁾ going to be “buried” would refer to some very small power plant of a few megawatts (MW): rather, pure CO_2 (meant for the production of mineral water or beer) is pumped underground, and this is a difference which probably matters: while pure CO_2 is capable of attacking carbonate rocks when

26) Practically, power plants which do not release more than $100\text{ g CO}_2/\text{kWh}$ (electrical energy basis) into the atmosphere are considered free of CO_2 emissions. If no retention is attempted, a hard-coal-based power plant produces $\geq 700\text{ g CO}_2/\text{kWh}$ (electrical), that is, retention must be more

efficient than 85% or, quite comparable to the required extent of flue gas desulfurication. Estimates on CO_2 deposition efficiencies which can be effected at prices within the framework of emission certificate prices range up to 90%.

some water is present, it is far less corrosive than actual flue gas which both contains anhydrides of much stronger acids and can induce redox reactions also. These more difficult experiments are planned only for later. The present objective is to find out whether chemical changes in deep aquifers by addition of some 50 000 t/year possibly influence deposition (e.g., by the formation of some barrier materials) or the circulation of deposited CO₂ in the deep aquifer. Given all this, it is probably too far-fetched to already estimate the expenditure it would take to achieve CO₂ deposition on a large scale in this manner: nevertheless, the costs are expected to be about as high as those of making electrical energy by either coal or natural gas power plants, that is, several US-cents or €-cents per kWh. In terms of CO₂, it would be some 20 €/t, about the present price which CO₂ emission certificates command. Really, a doubling of prices for fossil fuel-based electric current need not be anticipated or feared for reasons to be explained below.

Apart from the above more general considerations and “natural” examples of options (1) and (8) – formation of gas hydrates in deep ocean²⁷⁾ and liquid deposition below ground – pilot plants in California and the North Sea give an idea of what is feasible. In either case or experiment, the flue gases of some fossil power plant were first treated as usual to remove N, S, dust and metals, then dried and cooled,²⁸⁾ pressure-liquefied and put into the sinks. In San Francisco Bay the outlet nozzle for liquid CO₂ was placed some 600 m below the surface, corresponding to a pressure of somewhat more than 60 bar. Although white lumps of CO₂ hydrate would form immediately outside the nozzle and sink to the ground, the alkalinity of seawater soon caused them to dissolve. They proved intolerable to local marine wildlife: either organisms could flee, like fishes and cephalopods, or would die soon.

In the North Sea – which, by the way, is too shallow to do this except for several deep spots and the inlets of Norwegian fjords – another approach was pursued: the pretreatment of flue gas was identical, but then the liquid was passed anhydrously into an abandoned gas deposit (Sleipner gas field, near Eastern Scotland). Until now, performance and retention are good.

Even now, with increasingly sharp criticism of nuclear power (see below), still not too cheap production of wind and biomass energies, and CO₂ emission licenses being an item of international trading (and even undergoing forgery), additional costs from that kind of treating CO₂-laden exhaust gases must still cope with effects of competition in a liberalized, international market for electric energy. There already is surplus production which may sometimes urge European electricity suppliers to “sell” this energy on the Leipzig-based electricity stock exchange place not for free, but for *negative* prices to get rid of extra current! Probably

27) At the Yonagaki Knoll site, CO₂ hydrate forms just a narrow intermediate layer between covering (mainly biogenic) sediment and “neat” liquid CO₂, probably less than 20 cm thick.

28) Compressing and liquefying CO₂ in this way effectively amounts to operating a high-performance heat pump, as

compression of CO₂ from ambient pressure to >70 bar in an adiabatic manner would cause to heat it from some 100 °C (373 K; after wet desulfurication) up to some 900 °C (!). Accordingly, the gross thermodynamic efficiency of such power plants would considerably decrease.

political decisions are needed to place IGCC and CCS technologies in the market actually even though emission trading requirements might accomplish some of the task. In addition, people notice possible CO₂ dumping sites as a public hazard, even more so than nuclear power plants, making acceptance difficult. On a global scale, emission trading might help. In the short run, there are regional and national differences given the efficiency problems in energy conversions seen in large developing countries on one hand and ongoing replacement of fossil fuels in energy production by renewable resources—which remove the problem altogether if, and only if, designed properly. Pathway (5) is attractive to economies with fairly limited energy consumption while there is a broad and sophisticated chemical industry, for example, in Switzerland. The peculiarities of photosynthesis then to be run in extensive, mineral-fertilizer-independent cultures combined with temperature and thus climate effects make method (6) rather tricky to handle. Only young plant cultures still growing will actually absorb any CO₂ while climax biocenoses like the Amazonian rainforest would not. In addition, what shall we do with the plants after CO₂ was bound? Combusting or feeding to aerobics again will return CO₂ to the atmosphere unless there is secondary deposition while copying the paleontological way of burying them to get fossil fuels sooner or later probably would not be considered acceptable.²⁹⁾

An estimate of actual costs thus is difficult right now, but quite a number of approaches are at hand, with method (8) obviously preferred.

4.1.2.4 CO₂-based Radiative Forcing versus Other Sources and Distributions of Waste Heat: What about Nuclear Energy?³⁰⁾

Nuclear power plants do not emit CO₂ during their regular operation while, of course, mining uranium, processing the components and so on are linked to some CO₂ emission (some 30 g/kWh). However, their efficiency is considerably lower than with fossil-fuel power plants some 30% rather than about 50% because the very interior structures—from zircalloy fuel rod claddings over rod positioning grids up to the installations of the primary coolant cycle—of a reactor must not be heated much beyond 800 °C while the combustion chamber of a coal power plant might well stand 1300 °C. According to Carnot, the efficiency η hence is much lower. Comparing different kinds of power plants which deliver 1300 MW (el)—the typical size of a nuclear power plant will give away the following amounts of waste heat (in MW), with the latter mainly being passed into rivers in the case of nuclear power plants:

Combined gas-turbine plants	some 1050 MW
Hard coal power plants	1500 MW
Recent lignite PP	1700 MW
Old-fashioned lignite PP	>2000 MW
Nuclear power plant	close to 3000 MW

29) By now, the atmosphere contains more carbon than the presently living biota (760 versus 610 Pg), with fossil fuels (mainly coal) + peat, soil organic matter still

residing in the upper and middle Earth crust representing three to four times this amount (some 2000 Pg).

30) See also Section 4.4.

With this waste heat passed into rivers, aquatic creatures are exposed to temperatures to which they are not accustomed in moderate climates, causing a massively enhanced rate of metabolism, while the amount of dissolved oxygen decreases considerably. Even if they do not really run short of oxygen and die or are outcompeted by tropical species often introduced into our rivers and lakes, these water bodies may become anoxic in such summertime conditions. The water temperature in inflowing water for cooling purposes is also limited to 26°C in central Europe for technical reasons (besides those of aquatic ecology). As a result, during hot summer 2003 nuclear power plants all over central Europe, from France to Lithuania, had to be shut down and disconnected from the electricity grid simply because cooling waters in rivers got too warm. Quite obviously this has something to do with reliability of support . . .

Accordingly, nuclear power plants also suffer from greenhouse effect caused by consumption of fossil fuels and leakages of natural gas during mining, transport, and processing or by periodic increases of the solar constant whereas wind power plants benefit from this (larger T differences = larger average wind speeds³¹⁾).

4.1.2.5 Conclusion

Photosynthesis alone cannot cope with the additional burden of CO₂ passed into the atmosphere by anthropogenic combustion activities, as is obvious from the finer structure of Keeling's curve. Hence, as transition into a fully regenerative mode of electricity production will still take several decades to come, uncontrolled emission of CO₂ into the atmosphere must be avoided. For this end there are quite a number of different strategies, including both scavenging C before it undergoes actual combustion as well as deposition techniques at end of pipe, after combustion. The well-designed growing of vegetation may produce a limited³²⁾ buffer also

31) If there was no atmosphere around Earth, the average temperature produced by absorbing some 64% of the extraterrestrial solar constant of 1380 W/m² on a rotating spherical body would be 255 K (−18°C), corresponding to a blackbody radiation flux of 220 W/m². The actual value before large-scale industrialization was some 288 K, and in the near future global average is going to be some 291 K (at least), while (blackbody) radiation intensity increases with the fourth power of absolute temperature. Hence the change of radiation penetration will change from $(255/288)^{-4}$ to $(255/291)^{-4}$, that is, radiative retention ("forcing") increases from some 38 to 41% of surface IR flux, that is, by 3% or some 6.5 W. Of this change, about half is due to CO₂ increase, with the remainder produced mainly by water vapor, N₂O and CH₄. The net amount of radiative forcing due to additional CO₂ is about 1.5 W/m², or 750 TW globally. While by now some

2 TW_{el} of power plant potential are available, the additional gain of wind energy is considerable larger than this, and some 3 TW of direct waste heat are produced, with hundreds of times this value due to the greenhouse effect. Hence there is considerable amplification. Things are quite different with nuclear power plants: heat injections into rivers occur on a very small area, rather a line in the landscape, and critical effects can thus be produced readily without greenhouse amplification also.

32) All the fossil fuels now present in the upper crust, plus the amounts already ignited, which were formed over hundreds of millions of years, correspond to the photosynthetic turnover of just some 400 years. Accordingly, CO₂ removal by "burying" photosynthetically produced biomass in sediments never was really efficient.

but all the CO₂ still to be expected from further exploitation of fossil fuels can be allocated neither to vegetation nor to residual cavities from fluid fossil fuel productions. Probably such deposition is affordable; besides of legislation initiatives—up to the global scale—there also is engagement by institutions which directly feel possible effects of climate change. The most influential players of the latter kind are the large re-assurance companies like Munich Re. They have departments exclusively devoted to studying, predicting and scaling (in terms of insurance risk assessment) corresponding impacts for years now.

4.2

Soils and Sediments

4.2.1

Phytoremediation³³⁾

4.2.1.1 The Problem

Bioremediation (i.e., green technologies or phytotechnologies when relied upon plants) mainly deals with biological interventions aimed at environmental contamination assessment and alleviating pollution. Both industrialization and natural resource extraction resulted in the release of large amounts of toxic and waste compounds into the biosphere. These pollutants belong to two main classes: inorganic and organic ones. According to European Environment Agency (EEA) estimates, 1.4 million areas are contaminated (Puschenreiter and Wenzel, 2003). In India alone there are about 20 000 abandoned mine sites covering about 60 different kinds of minerals. Biological interventions mediated by some wide array of biological species (none of which will be able to “remove everything”) can be used to remove unwanted compounds from the biosphere, thus contribute significantly to the fate of toxic spills.

Phytotechnologies deal with the use of plants in pollution control and removal as well as on aspects related to plants from polluted environments as a source of food, fodder, fuel and fertilizers. Plants are able to indicate, exclude, accumulate, hyperaccumulate or metabolize toxic inorganic or organic substances. Thereby they contribute significantly to the fate of chemicals, and they can be used to remove unwanted compounds from the biosphere. Further, chemicals can enter the food chain via plants, which cause unwanted/causing harmful effects (Schroeder and Schwitzguébel, 2004).

As of May 2009, about 10 684 articles have been published on various aspects of bioremediation, starting with only 11 in 1989 (Figure 4.19). Thus, there has been a steep rise in scientific investigations and a real knowledge explosion in green technologies. An environmental watchdog survey revealed that sites in Russia, China and India are among the “top ten” most polluted places/countries in the world (Anonymous, 2007). In the developed nations as well as developing nations there have been convincing evidence for applications of green technologies.

33) According to Prasad *et al.* (2010).

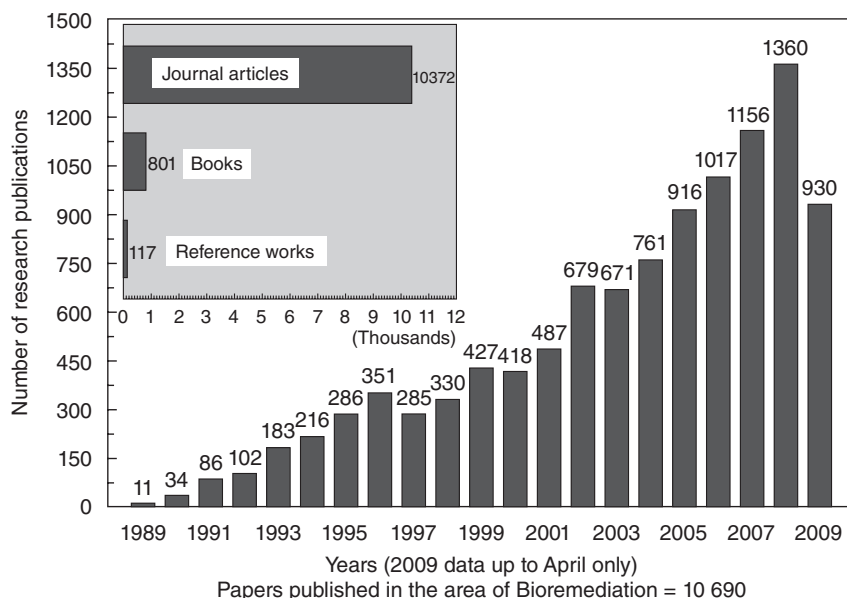


Figure 4.19 Articles published on bioremediation (based on www.sciencedirect.com).

Therefore, the field of bioremediation belongs to the realm of environmental biotechnology and is not to be confused with biodegradation, which tackles the biological bases of the (mostly bacterial) metabolism of unusual and/or recalcitrant compounds. Depending on the degree of such intervention, bioremediation is generally considered to include natural attenuation (which entails little or no human action), or bio-stimulation (requiring the addition of nutrients and electron donors/acceptors to promote the growth or metabolism of certain microorganisms), or bio-augmentation, the deliberate addition of natural or engineered microorganisms with the desired catalytic capabilities.

4.2.1.2 Purposes of Mitigation of Noxious Effects

Bioremediation is exploitation of biological interventions of biodiversity for purposes of mitigation (and wherever possible complete elimination) of the noxious effects caused by environmental pollutants in a given site (Figure 4.20). If the process occurs in the same place which was afflicted by pollution then it is called *in situ* bioremediation. In contrast, deliberate relocation of the contaminated material (soil and water) into a different place to intensify biocatalysis, is referred to as *ex situ* treatment. Biodiversity is the precondition for bioremediation. Quite a variety of plants, natural, transgenic, and/or associated to rhizosphere microorganisms are extraordinarily active in these biological interventions cleaning up pollutants by removing or immobilizing. Diverse microbes are the most active agents, fungi and their strong oxidative enzymes are key players in recycling

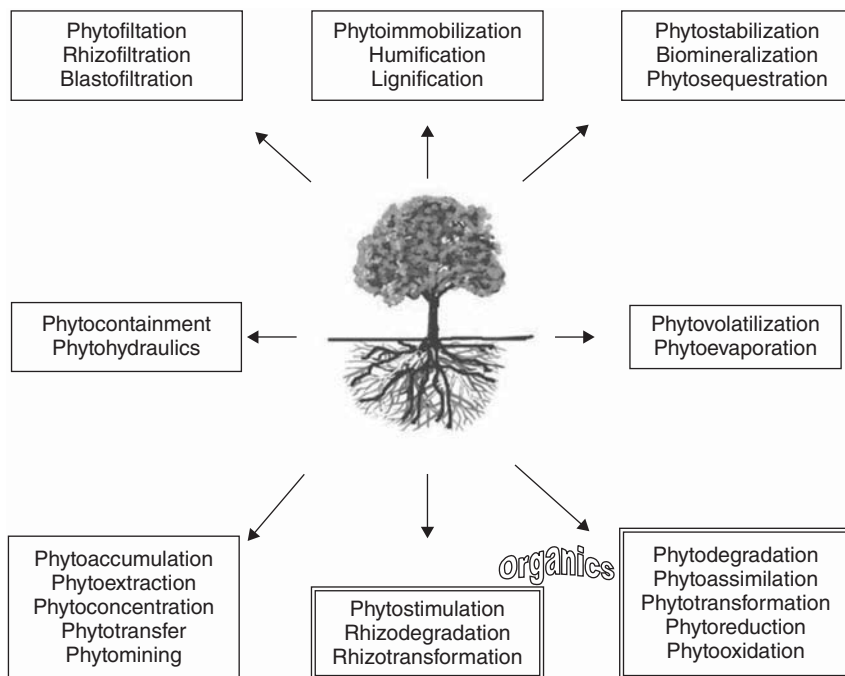


Figure 4.20 Selected bioremediation processes involving some wide scale of biodiversity (for more details on the transformation, control and containment of contaminants see McCutcheon and Schnoor, 2003).

recalcitrant polymers and xenobiotic chemicals as well (Loeffler and Edwards, 2006; Kawahigashi, 2009).

Phytoremediation can be used in combination with other traditional and innovative remediation technologies. Cleanup can be accomplished to certain depths below ground level, within the reach of plants' roots. Such sites need to be maintained (watered, fertilized, monitored). Phytoremediation may yet be slower than mechanical cleanup methods such as excavation and proper disposal and is limited to soil depths that are within the reach of plants' roots. Phytoremediation can, however, be used in combination with other remediation technologies.

Plant physiology, agronomy, microbiology, hydrogeology and engineering are combined to select the proper plant and conditions for a specific site. Phytoremediation is a procedure that can reduce remedial costs, restore habitat and clean up contamination in place rather than entombing it in place or transporting the problem to another site.

Phytoremediation is the use of certain plants and trees to clean up soil and water contaminated with metals and/or organic contaminants such as solvents (Schwitzguébel *et al.*, 2011), crude oil and polyaromatic hydrocarbons (PAHs). Phytoremediation is an esthetically pleasing, solar-energy driven, passive technique that

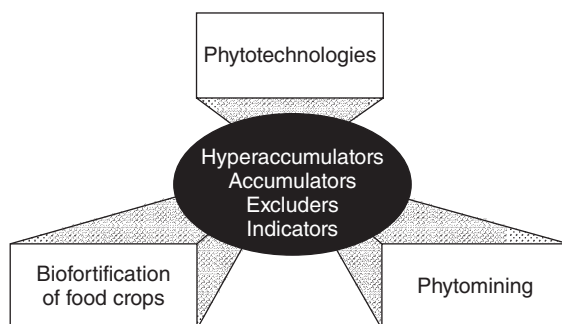


Figure 4.21 Beneficial use of plant–metal interactions: (i) phytoremediation, (ii) biofortification of food crops and (iii) phytomining. The desirable traits are: high tolerance to contaminants, hyperaccumulation, wide ecological amplitude, easy management, economics and value additives, fast-growing and high biomass producing plants, such as *Salix* and *Populus* spp. *Indicator*: Plants in which uptake and

translocation reflect soil metal concentration and exhibit toxic symptoms. *Accumulator*: Plants in which uptake and translocation reflect soil metal concentration without showing toxic symptoms. *Excluder*: Restricted uptake of toxic metals over a wide range of soil metal concentration. *Hyperaccumulator*: Plants in which metal concentration is up to 1% dry matter (this is metal dependent, most often Ni or Zn; Baker, 1981; Markert, 1996).

can be used along with—or, in some cases, in place of—mechanical cleanup methods at sites with shallow, low to moderate levels of contamination.

Thus, phytoremediation of contaminated soils offers an environmentally friendly, cost effective and carbon neutral approach for the clean-up of toxic pollutants in the environment. Plants with the ability to hyperaccumulate, accumulate, exclude and indicate heavy metals are important in environmental remediation (Figure 4.21).

4.2.1.3 The Use of Certain Plants and Trees to Clean up Soil

Plants with the ability to take up volatile organic compounds and sequester pollutants have been proposed as a solution to the treatment of toxic contamination *in situ*. However, the use of plant-based technologies has a number of limitations, primarily due to the fact that plants are autotrophic and not ideally suited for the metabolism and breakdown of organic compounds. One of the major limitations with current phytoremediation is the often slow timescale for remediation to acceptable levels and also toxicity to the plants themselves. To some extent, this can be addressed through interactions with the natural microflora associated with plants; endophytic bacteria, rhizosphere bacteria and mycorrhizae have been shown to have the potential to degrade organic compounds in association with plants (Dowling and Doty, 2009; Weyens *et al.*, 2009; Figures 4.22–4.24).

The use and transformation of over 100 000 individual compounds whose current locations are largely unknown have resulted in the establishment of new fields of research, which have one thing in common: they link ecological, physiological and chemical/analytical lines (Markert, 1996; Markert *et al.*, 2008). This

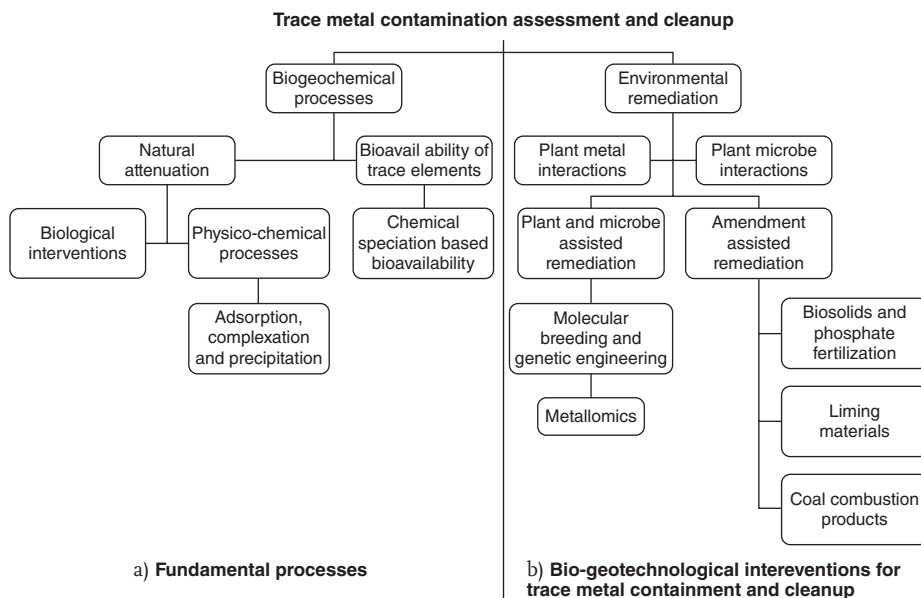


Figure 4.22 Biogeochemical processes and enhanced remediation to mitigate environmental contaminants and pollutants (Prasad *et al.*, 2010).

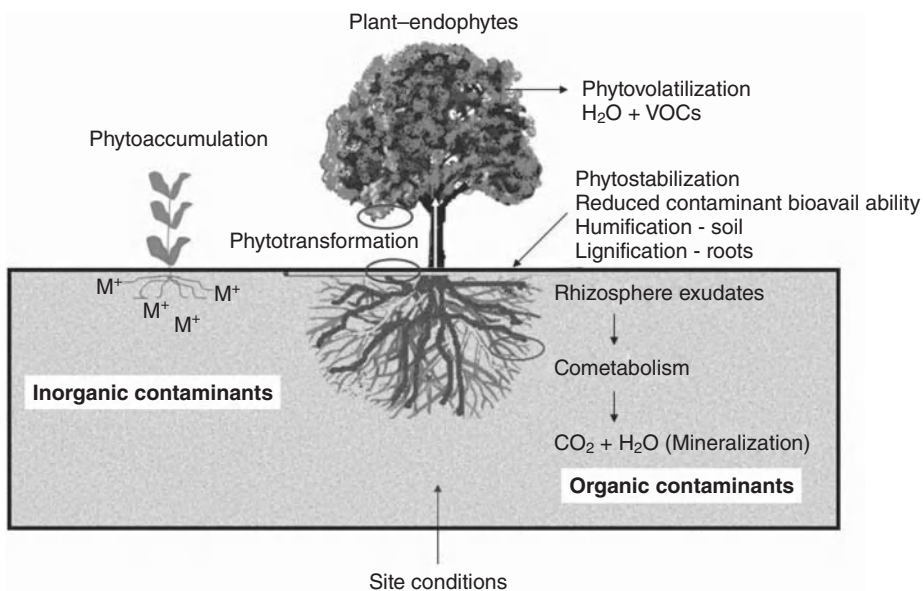


Figure 4.23 Plant–rhizosphere interactions (including plant–endophyte relationships) in environmental decontamination (for more details see Weyens *et al.*, 2009).

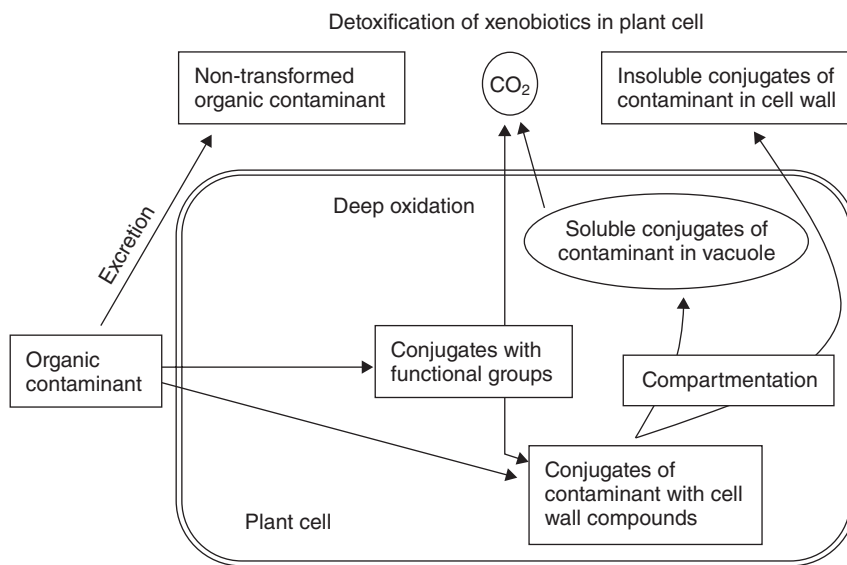


Figure 4.24 Detoxification of xenobiotics. Pharmaceutical residues are common contaminants of ground water in many cities [based on COST action 859, Szeged (Hungary) workshop presentations; Prasad *et al.*, 2010].

complex system of interactions and interrelations requires intensified efforts to provide integrated information on the status and development of environmental quality. Bioindicators and biomonitors have proven to be excellent tools in many of these cases and could provide information which cannot be derived from technical measurements alone (Markert *et al.*, 2003a; Prasad, 2008; Section 4.4.1). Bioindicators and biomonitors yield extensive information. Thus an increasing knowledge of ecology gave way to the insight that organisms, cells and subcellular compounds likewise can be used as indicators for ecosystem qualities and for assessment of the impact of environmental stress on the composition and functioning of ecosystems. Indicators can be used to assess (environmental) quality, but also to investigate trends, for example, monitoring systems with measurements to be repeated in time, what is of highest interest with respect to any phytochemical method in use.

Biotechnology and systems biology approaches are gaining considerable importance in fostering bioremediation (de Lorenzo, 2008; Van Aken, 2009). It is strongly believed that there are three dimensions for the effectiveness of vital bioremediation process, that is, chemical landscape (nutrients, electron donors/acceptors and stressors), abiotic landscape and catabolic landscape of which only the catabolic landscape is “genuinely” biological. The chemical landscape has a dynamic interplay with the biological interventions on the abiotic background of the site at stake. This includes humidity, conductivity, temperature, matrix conditions, redox (O_2) status and so on (de Lorenzo, 2008).

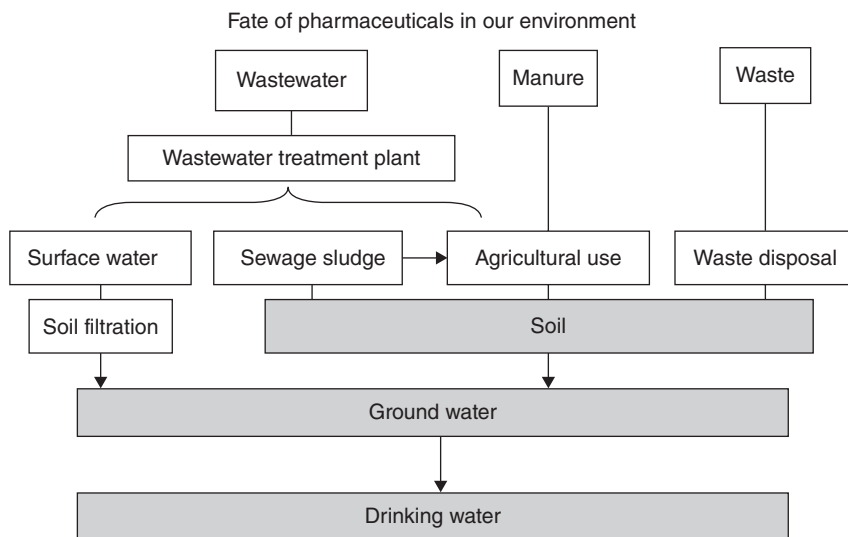


Figure 4.25 Degradation of pharmaceuticals (and other organic compounds capable of or meant to attack microorganisms including those in soil after their disposal into the environment along wastewater disposal and cattle breeding. In the very end, compounds

which are refractory may show up in drinking water again [including steroids such as ethinylestradiol (EE2)] [based on COST Action 859 workshop presentations, Szeged (Hungary); Prasad *et al.*, 2010].

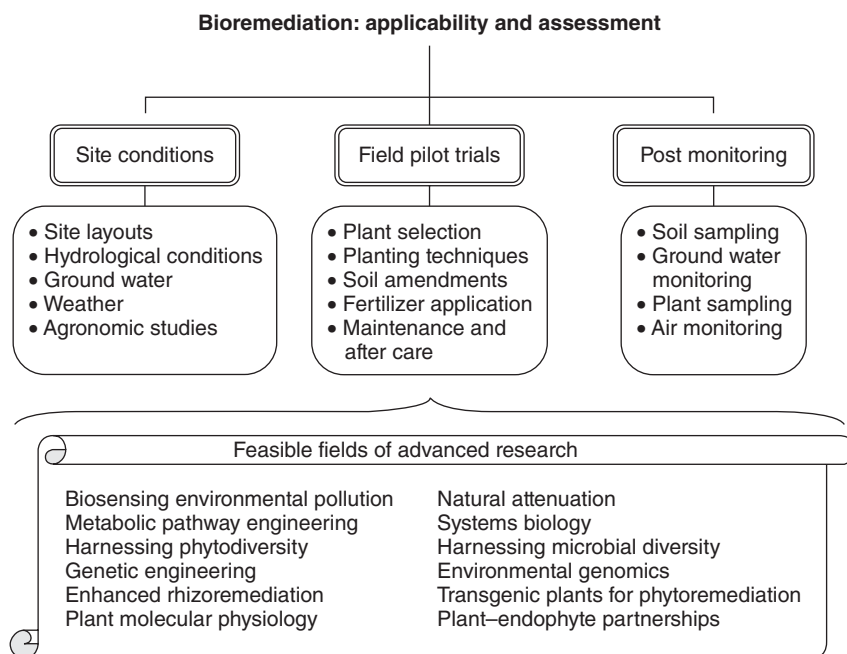
4.2.1.4 The Efficacy of Bioremediation Has Been Determined Chemically

Conventionally the efficacy of bioremediation has been determined chemically, by measuring changes in total pollutant concentrations usually by an assemblage of sophisticated instruments. However, recently attempts have been made to use biosensors, especially microbial whole-cell biosensors to monitor pollution (Figure 4.25).

Information is encoded in deoxyribonucleic acid (DNA) and transferred through ribonucleic acid (RNA) to ribosomes to make proteins or enzymes which are used to operate systems within the organism. In this regard enzymes are responsible for the degradation of organic contaminants which is used by the bacterial cell to produce both the building blocks of life and energy. The degradation of any organic molecule, including contaminants, requires the production and efficient utilization of enzymes (Table 4.2), as a rule. In some instances, degradation is merely a complex oxidation/reduction reaction. The electrons or reducing equivalents (hydrogen or electron-transferring molecules) produced must be transferred to a *terminal electron acceptor* (TEA; bacteria are grouped into three categories, namely aerobes, facultative aerobes/anaerobes and anaerobes). Herbicide phytoremediation using transgenics is one of the most successful examples. Transgenic plants engineered for the transformation of explosives and metabolic pathway engineering for degradation of xenobiotics are in progress (van Aken, 2009).

Table 4.2 Selected enzymes capable of degrading organic contaminants (Husain, Husain and Kulshrestha, 2009).

Enzyme	Target pollutant	Examples of plants
Dehalogenase	Chlorinated solvents	<i>Populus</i> , <i>Myriophyllum spicatum</i> , <i>Nitella</i> , <i>Spirogyra</i> , <i>Anthoceros</i>
Laccase	Explosives	<i>Nitella</i> , <i>M. spicatum</i>
Nitroreductase	Explosives	<i>Populus</i> , <i>M. spicatum</i> , <i>Lemna minor</i> , <i>Nitella</i>
Peroxidase	Phenols	<i>Armoracia rusticana</i>
Phosphatase	Organophosphates	Duckweeds
Cytochrome P450	Xenobiotics (PCBs)	<i>Brassica</i> sp.

**Figure 4.26** Knowledge explosion in the field of bioremediation—progressing fields of advanced research (Prasad *et al.*, 2010).

4.2.1.5 Conclusion

Much progress has been made in the field of bioremediation in Europe and North America. The costs, benefits and residual risks thereafter need to be investigated to present the final outcome to the decision makers. Further, particularly countries with vast biodiversity and high environmental pollution must implement and evaluate the exciting and feasible biotechnological options. The obvious approach to address some of the aforesaid limitations is the application of recombinant DNA technology to express specific genes from heterotrophic organisms such as bacteria and mammals to increase plant tolerance for metabolism of organics and decontamination of inorganics such as toxic trace metals (Figures 4.26 and 4.27; Scow and Hicks, 2005; Singh *et al.*, 2008; Wood, 2008; Abhilash, Jamil and Singh, 2009; Ruiz and Daniell, 2009).

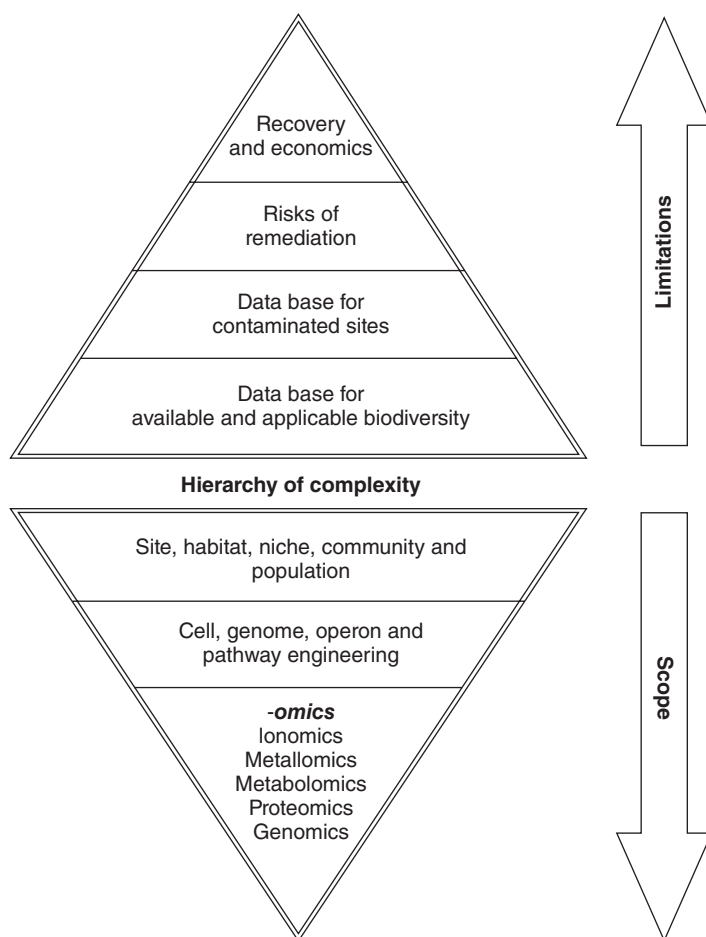


Figure 4.27 Scope and limitations of bioremediation—the hierarchy of complexity (de Lorenzo, 2008; Van Aken, 2009).

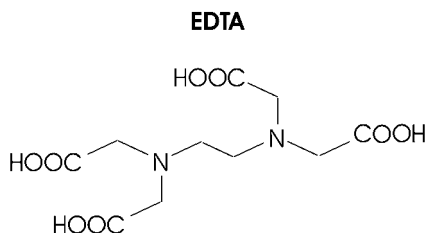


Figure 4.28 The structure of ethylene diamine tetraacetic acid (EDTA): a symmetrical, hence achiral, tertiary amino acid (each N atom binds three substituents other than H).

4.2.2

Ethylenediamine Tetraacetic Acid—Its Chemical Properties, Persistence, Ecological Hazards and Methods of Removal

4.2.2.1 The Problem

Ethylenediamine tetraacetic acid (EDTA; Figure 4.28) is often used both in domestic (washing,³⁴) laundry detergents, deodorant sticks or lotions) and commercial applications (concrete preparation, etc.) due to various features of its being an effective, up to hexadentate³⁵) complexing ligand. By complexation, reaction pathways and concentrations and reaction kinetics of coordinated (ligated) metal ions can be precisely controlled, both precluding precipitation of (alkaline earth) salts (water softening) and slowing down their formation during concrete solidification. Being excellently soluble in water and escaping microbial decomposition, EDTA makes it through process waters and sewage treatment plants into the aquatic environment. The very chemical properties of EDTA which are used in closed or semi-closed systems (i.e., its persistence while being an efficient metal ligating agent) then pose problems in terms of ecotoxicology once EDTA gets into the free (aquatic or soil³⁶) environment.

The size and extent of these ecotoxicological hazards is partly still a matter of debate. Notwithstanding this, very sizable amounts of EDTA and similar synthetic

34) In shower shampoos, hair shampoos or deodorants, it is now often replaced with similar compounds like 1,2-cyclohexanediamine tetraacetate and so on, the persistence and biodegradability of which sometimes still remain to be demonstrated more benign to the environment than those of EDTA.

35) Whereas the formally octadentate higher homolog diethylene triamine pentaacetate (DTPA) normally keeps at least six metal coordination sites occupied, EDTA is more flexible, with many octahedral $[M(edta)]^{n-}$ complexes taking up additional ligands (both mono- or bidentate anions and neutrals like NH_3 , RNC or CO) by cleaving

one M-N- or M-carboxylate linkage to “accommodate” the additional ligand, producing stable $[M(edta)L]^{n-}$ ions.

36) While the upper root region serves to block further transport of certain toxic metal ions in various plant species because: (i) re-ligation by xylem-borne chelators (which are poorly characterized by now) after rhizosphere absorption of citrato-, malato-, oxalato- or amino acid complexes of, for example, Cd^{2+} fails or (ii) these metal ions get locked up in the xylem by forming insoluble phosphates, this protection mechanism (both to the upper parts including photosynthetic organs of the plant and to its consumers)

amino acids are used, of which but the share which is consumed in cement manufacturing and processing can be expected to keep away from hydrosphere and biosphere almost permanently. All that is consumed otherwise is likely to actually hit the environment rather sooner than later. Accordingly, the problem will consist of three different parts or issues:

- How, and to which extent, will EDTA influence the environment? Does it for example, mobilize heavy metal ions from aquatic sediments, and if so, under which conditions (including pH, ions present in water, illumination, presence of HPO_4^{2-} , etc.) this is going to happen and become relevant in ecotoxicity?
- How can this rather stable and microbiologically inert substance be degraded without producing additional damages by secondary products or applied reagents?
- Can EDTA be replaced by other agents?

4.2.2.2 Fields and Amounts of EDTA Application

Early in this century, some 60 000 t/year of EDTA³⁷⁾ and its (mainly alkali and Ca) salts were consumed in the EU, with the largest share of 40% used in making paper and cellulose in Scandinavia (i.e., Sweden, Denmark and Finland). In earlier days, before starting to phase out EDTA (itself being a substitute for polyphosphates in water softening) for washing and laundry purposes, the consumption was even higher. EDTA will coordinate Ca^{2+} or Mg^{2+} ions, precluding precipitation of the respective carbonates from “hard” water. In this purpose EDTA replaced polyphosphates, reducing effects of eutrophication in open waters connected to sewage water treatment while, however, introducing an agent which can massively alter biogeochemical cycles of metals, which will be explained in more detail below. Hence, there is ecotoxicological ambiguity with EDTA or, to put it bluntly, its application will be safe and acceptable only when considering various and sometimes complicated environmental conditions. Even though, some one-third of EDTA consumption (and that of its salts) still is related to commonly unspecified, mainly industrial applications in detergents. While EDTA application in photography was phased out along with the decline of AgHal-based films getting more and more replaced by digital electronic storage systems, it was and still is even allowed as a food additive: food additive E 385 (which remains on the European Union list of accepted additives) is the complex salt $\text{Na}_2[\text{Ca}(\text{edta})]$.

will fail if EDTA is added to the soil solution: then metals like cadmium form complexes which can no longer undergo oxidative ligand exchange in the upper root parts (cf. Fränzle, 2010) but proceed all the way up into leaves (needles) and fruits, for example, with Cd^{2+} + EDTA in corn (*Zea mays*). This is fine for phytoremediation by using these plants but possibly fatal if other uses are intended.

37) Here, adhering to the common practice, EDTA (large letters) denotes the free acid obtained by protonation of the anion $(\text{edta})^{4-}$, that is $\text{EDTA} = \text{H}_4(\text{edta})$. Although EDTA is a fairly strong acid ($\text{pK}_{\text{a}1} = 2.13$), protonation of one of two amino groups to produce $\text{H}_5(\text{edta})^+$ still is feasible in aqueous acids. EDTA and $\text{H}_5(\text{edta})^+$ might actually be zwitterions, depending on the solvent.

There is another application which directly draws on the hard degradability of EDTA: as a smell-preventing agent in deodorant sticks. How does this work? In fact it does because EDTA—being a tertiary amino acid—cannot be degraded in the same way as primary or secondary ones by oxidative decarboxylation.³⁸⁾

Human sweat contains many salts of both light and heavy metal ions (Mg, Zn, Fe . . .), besides organic acids and other reduced organics. Bacteria which feed on these organic compounds present on human skin also make use of the metals abundant in sweat to construct their own metalloproteins during metabolism and budding. Among the metabolic products metabolized by these bacteria butyric (butanoic) acid is the most prominent for its noxious smell. Now consider the effect of EDTA addition: as we noted before, bacteria dwelling on human skin will require Fe, Zn, Mg like almost every other organism³⁹⁾ does while EDTA does form so stable complexes that it effectively precludes formation or maintenance of corresponding metalloproteins. Hence, complexation of the above essential metals by EDTA makes life, let alone reproduction, impossible for these bacteria. Hence: no metal ions bioavailable from sweat, no growth of local bacteria, no smell of decomposing sweat.

Here it is the aim to block biochemical transformations promoted by metalloproteins by destroying the latter upon EDTA addition, but usually we are concerned with just the opposite aim: what happens if we try to degrade something in, say, a digestion tank or some other apparatus for biotreatment of hazardous organics while EDTA is present? Obviously, effects should be most grave if enzymes operate outside of cells while drawing upon metal ions which are not too strongly bound but readily react with EDTA. Typical exoenzymes present in soil or/and rotting wood and litter include exoperoxidases (fungal, Mn + Fe), monoamine oxidases (Cu), hydrolases (Zn), and cytochrome oxidases (Fe + Cu). Unless the enzymes are protected from EDTA attack by the latter being “filled up” with Mg²⁺ or Ca²⁺ ions (sea water, marl soils, etc.), degradation of both the above “natural” substrates in litter layers and anthropogenic components (e.g., phenols, Cl-PAHs) will be highly compromised, even in aerobic conditions. As a result, turnover of plant organic matter is slowed down, making litter pile up, with quite a number of predictable consequences from rather more likely anaerobic conditions

38) For the pathway of hydride transfer and N cleavage by vitamin B₆. After having taken up both H and N, with pyridoxal phosphate being converted into pyridoxamine (while metals are not required in this process; Metzler, Ikawa and Snell, 1954), pyridoxal phosphate is regenerated by passing both components to some α -oxo acid as an acceptor. In animals, this acceptor is 2-ketoglutarate which thus affords glutamate whereas in plants, glyoxylate HCO-COO⁻ is converted into glycine. Secondary amino acids like proline and hydroxyproline can be

processed this way, and likewise iminodiacetate but not NTA, EDTA, or DTPA, let alone quaternary ammonium salts.

39) Zn apparently is essential to all forms of life we know; several insects and moulds can do without Fe whereas there is a remarkable group of sediment-dwelling mesoscopic animals (Loricifera) which would survive without Mg if in aerobic conditions (Danovaro *et al.*, 2010) but need it while living in permanently anaerobic conditions (!).

in intermediate soil layers—damaging plants—up to an increased likelihood of forest wildfires.

There are technical applications of EDTA where turnover of metal ions into solid compounds is controlled by the metal being added as an EDTA complex which then slowly decomposes. Here, some $[M(edta)]^{n-}$ gives away small but well-defined amounts of M^{x+} per period of time.

EDTA complexes which are kinetically labile, thus capable to give away their central ions if slowly can be used as reservoirs for metal ions in chemical reactions, and actually this is now the main (by amount) application of EDTA in the European Union: when some complex $[M(edta)X]^{n-}$ slowly releases well-defined concentrations of metal ions into a mixture where subsequent reactions consume these very metal ions (e.g., during hardening of concrete), or get removed from the mixture for example, by electrochemical means (galvanic technology), it is possible to control these reactions as just a limited and rather constant concentration of “free” metal ions is present all over the time of the process. Thus, EDTA added to some component of cement will cause both slower and better [formation of larger crystal needles, making concrete more stable toward pressure (very high buildings, dams!)] hardening⁴⁰⁾ of concrete. Thus building concrete structures did recently become one of the main applications of EDTA. Other applications likewise make use of the complex ligand properties, be it in removing abundant heavy metal ions from water $[Fe(III), Mn^{2+}]$ which otherwise could cause stains in textiles [citric, oxalic, (proteinogenic) amino acids could also be used but form less stable complexes] or formerly in photographic developing liquids (removing remanent unphotolyzed Ag^+ ions, here replacing ammonia, thiosulfate, etc.). Applications in making cellulose from wood (Kraft pulp leaching by sulfite + EDTA) is disallowed in Germany and many other states for its hazards to water but was broadly used in Scandinavia, Russia, Korea and elsewhere.

40) Otherwise constructions like the skyscraper Burj Khalifa (Dubai, 828 m tall) would not be feasible: concrete taken for such purposes must remain sufficiently liquid long enough as to pump it to these heights after mixing the components even at outer temperatures near 50°C, while then withstanding shear pressures of >250 bar owing to the mere weight of the upper storeys of the building. Among the principal elements in concrete (Ca, Al, Si) the two former ones produce a crystalline compound (grossite, $CaAl_2O_7$) which takes the shape of long crystal needles. As these needles point are rather long and point into different directions, aggregates will form which have substantial stiffness against both shear, distortion and torsion and lend this mechanical stability to the silicate matrix they are embedded in.

EDTA coordinates both Ca^{2+} - and Al^{3+} ions, hence the average levels of free ions are rather low. While grossite will still form, crystal growth will be much slower and giving a better arrangement, making the concrete more smooth to work with and mechanically more stable after hardening. As noted before, slower hardening offers many advantages especially when erecting building in hot climates; sometimes it is the only way to get concrete into sophisticated shapes completely, as are increasingly required both by architects wanting to attract interest for their constructions and likewise by technical concrete items—including ship vessels, parts of power plants and tunnel segments “anchored” in shattered surrounding rocks.

4.2.2.3 The Compound and Its Properties: Why a Complexing Agent Makes Trouble

As the anion, not already having absorbed metal ions, EDTA is going to bind these metals so strongly that it can remove them even from the centers of metalloproteins. Hence, treating metalloproteins with EDTA will block its own possible degradation. Things are different when EDTA did already form some metal complex; given this, it is both degradable to some extent by microbes and even an accepted (registered, allowed) additive for foods in the European Union [$E_{385} = Na_2Ca(ETDA)$].

The examples of Al(III) and Cu(II) already give proof that complexation by EDTA is not limited to “harmless” metal ions but can leach others, toxic ones from either soil or aquatic sediment, into green plants. Then $[M(edta)]^{n-}$ complexes can make it beyond the rhizosphere/xylem barrier which would not accomplish this otherwise, for example, Cd in corn (cf. the statements on phytoremediation), rare earth elements (including radioactive fission product isotopes of Y, La, Ce, Pm, Sm, Eu) in wheat, open water columns, springs, or wells if EDTA (or similar agents) are “free” to ligate and mobilize corresponding ions by chelate⁴¹⁾ formation. The activity of soil-borne EDTA in dispersal of radionuclides (^{60}Co) was demonstrated rather early (Means, Crerar and Duguid, 1978) and even then assumed to extend to other fissiogenic radionuclides, like rare earth elements (ibid.). EDTA being highly polar, most hydrophilic and readily forming H bonds, it will get into open waters—after escaping both adsorption (for being too polar) and microbial degradation in sewage treatment plants, the stability of its complexes bears a potential—and risk—to extract various metal ions from limnetic⁴²⁾ sediments [the extraction (rates or efficiencies) can be increased by applying ultrasound to the sediment under an EDTA or citrate solution (Hwang, Park and Namkoong, 2007), and this possibly occurs also under impact of surf]. This risk is largest in “soft” (containing but traces of alkaline earth ions), metal-poor fresh waters.

All EDTA, ethylene diamine triacetate, nitrilotriacetate (NTA) and diethylene triamine pentaacetate (DTPA) will produce various complexes with heavy metals—whether they are absorbed from solution or sequestered from the underneath sediments—some of which now are photosensitive (cf. methods of removing

41) The term “chelate” is derived from (old) Greek *chele* = pincer of a crab. A chelating ligand will arrange around some metal ion in much the same manner as the pincer of a crab or lobster does, by binding by several atoms rather than a single ion to this metal ion. By forming some ring or even several rings (tridentate or higher polydentate ligands, e.g., citrate, iminodiacetate) including the metal ion, the do not only bind much more strongly to the metal than a single-atom (monodentate) donor (e.g., F^- , CN^- , NO , SPh^-) would or actually could, but in

addition construct a rather rigid structure in space. Hence it often is difficult to remove some chelating ligand once again after binding except they can be oxidized to produce non-ligands (e.g., oxalato ligands to CO_2).

42) Because in seawater concentrations of alkaline earth ions Mg, Ca, and Sr are several times larger each than in “reference freshwater” (Markert, 1994a), EDTA in the ocean will be “occupied” by about 100% by these ions even though the complexes are not too stable.

EDTA) while others are not. This is important to understand the reactions to follow in the environment.

Metal ions which form complexes to decompose photochemically via ligand to metal charge transfer (LMCT) states like Fe(III), Co(III), Mn(III), Ce(IV) first produce less stable (with respect to the EDTA-based speciation forms) $[M^{\text{red}}(\text{EDTrA})]$ complexes⁴³⁾ which then can hydrolyze, releasing the (reduced) metal ions which then are readily bioavailable. Thus they become toxically relevant also.⁴⁴⁾ While other ions like Cd^{2+} , Pb^{2+} are also extracted from the sediments in these circumstances, their EDTA complexes will rather persist and become absorbed by aquatic life forms as such as these complexes are photochemically inactive (inert) in the tropospheric solar spectral range.

When EDTA uses all of its six possible coordination sites (cf. Rocha, Rein, and Toma, 2002), it will “wrap” a main group or transition metal (*d*-series) ion completely, while rare earth elements or actinoid or early transition metal ions bring about higher coordination numbers and thus bind additional ligands. The metal ion thus gets a “storage form” ready to be absorbed by plants even beyond the rhizosphere. Hence an EDTA pollution of soil may translate into increased heavy metal burdens of edible plant parts in turn. However, complete coordination (CN = 6) also means that no⁴⁵⁾ other, additional metal ion, say one catalyzing photooxidation, may be additionally bound to EDTA. Hence complexes of the above toxic heavy metal ions are rather persistent. In well-aerated sediments and moderate climates EDTA lifetimes are given as 200–300 days irrespective of any metal ions bound to it. In anoxic soils, there is no trace of EDTA degradation after 50 days, hence the lifetimes must be of the order of many years.

- 43) M^{red} = reduced metal ion, here Cu(I), Mn(II) or Ce(III), while EDTA = ethylene diamine triacetate which is the primary photooxidation product of EDTA.
- 44) Recall that among speciation forms of heavy metals the “free” aquaions *tend* to be the most toxic ones, except, sometimes for fluorocomplexes and certain organometal species—if the latter are lipophilic and reasonably stable toward hydrolysis. Toxicologists made the *free ion activity model* (FIAM) out of this empirical observation. The FIAM rule also holds for metal ions like Cu^{2+} which form so stable complexes that free ions hardly occur in natural environments; here exactly this propensity to coordinate to “almost everything” spells massive metabolic disturbances, for example, the various fatal syndromes associated with an improper capability to control pathways and coordination sites of copper ions.
- 45) Tertiary amino acids which are more complicated than EDTA, and hence have

>6 possible ligation sites, like DTPA mentioned in the above text, their eight or more coordination sites might even accommodate two (two like or different) metal ions at one ligand molecule or polyanion, for example, Ca^{2+} *plus* one photochemically activating metal ion like Fe(III). Given this, the “terminus” of that large ligand which had bound Fe(III)—be aware that such large ligands need not be as symmetric as DTPA, for example, protein molecules!—will undergo partial photooxidation and hydrolytic dismantling. The reduced metal ion tends to slip out from this position which lost some coordination sites, leaving behind a Ca^{2+} complex of the ligand fragment which is photochemically inactive itself but somewhat accessible to microbial degradation now—degradation afforded secondary amino groups which can now be attacked by pyridoxal, for example.



Figure 4.29 An array of mesocosms at RWTH Aachen University, Germany. Mesocosms are used to investigate medium-sized (hence their name) biological systems (meant to mimic or represent smaller ecosystems). For example, the effect of certain environmental chemicals on some number of animal and plant species brought together in one aquarium tank may be studied. Besides aquaria, mesocosms can be constructed as, for example, ponds (like in

this picture), lysimeters, greenhouses and the like, which can either be open, exchanging matter with the free environment (then the balance is usually controlled by steady weighing, like in lysimeters) or be closed. Photograph courtesy of: Outdoor mesocosm facility at RWTH Aachen University (Germany), Research Institute for Ecosystem Analysis and Assessment (gaiac); photo by Tido Strauss.

Mesocosms in the laboratory and test ponds (Figure 4.29) are used to see whether there is actually heavy metal ion extraction from the sediment due to presence of EDTA in the water column. The latter is found only to occur if the EDTA concentration surpasses the sum of the heavy metal ions above sediment. It can be concluded that some part of EDTA must be “free” (just having undergone protolysis to form di- $\text{H}_2\text{edta}^{2-}$ or trianions Hedta^{3-} depending on local pH) of metal complexation to let this happen.

Reference fresh water⁴⁶⁾ (RFW) data (Table 4.3) show that mobilization of elements like lead and cadmium from sediment will mainly be controlled by the iron content of the water column above. Whereas Fe^{2+} may be present at mg/l levels, air oxidation and higher pH {simple Fe(III) amino acid complexes like $[\text{Fe}(\text{glyc})_2\text{Cl}]$

46) *Reference fresh water* (RFW; defined by Markert, 1994b) represents a weighted average from analytical data of unpolluted freshwaters which are spread over different continents and climate regions. For data, cf. Table 4.3.

Table 4.3 Concentration levels of various metal ions in reference fresh water (RFW; according to Markert, 1994b; Fränze and Markert, 2002a, 2002b) versus stabilities of their EDTA complexes (Mizerski, 1997).

Element	C _{RFW} (nmol/kg)	log C _{RFW}	−log <i>k</i> _{diss(EDTA)}	Coordinated?
Al	7400	−5.12	15.9	+
Ba	75	−7.12	7.8	(+)
Be	11	−7.96	8.7	(+)
Ca	50 000	−4.3	10.8	+
Co(II)	9	−8.04	16.3	+
Co(III)			41.1	+
Fe(II)	9000	−5.04	14.2	+
Fe(III)			25.2	+
Mg	164 000	−3.79	8.7	+
Ni	5	−8.30	18.7	+
Mn(II)	90	−7.04	14.0	+
Pb	14	−7.85	18.0	+
Zn	80	−7.10	16.6	+

The RFW according to Markert (1994b) excludes extreme values owing to either pollution or geochemical peculiarities. Thus a comparison with RFW data can be used to determine states of pollution.

precipitate Fe aquoxides at pH > 8.2; i.e., about marine conditions} can reduce these levels far below that of RFW by precipitating Fe₂O₃ hydrates. Typical values of EDTA in exhaust pipes of sewage water treatment plants are some 300–800 µg/l EDTA (1–2.7 µM/kg) while <20% underwent degradation whereas German rivers contain ca. 30 µg/l (0.1 µM/kg). Once the iron concentration is reduced to ≤2 µM/kg or below 0.1 µM/kg, extraction of other heavy metals from sediment will actually occur unless lots of Mg²⁺ or Ca²⁺ are present. The “normal” (i.e., RFW) Fe level is 9 µM/l. EDTA complexes of most heavy metals and of Al, Y, Be are so stable that the ambient metal concentrations in fresh water suffice to cause complexation by EDTA.

Iron (namely, the trivalent form), aluminum, lead, cobalt, nickel, and zinc are distinguished by the largest stability excesses of EDTA complexes as compared to their respective RFW levels (Table 4.3) while sizes of these “extents” are rather similar to each other. As a result, the distribution of these metals in an excess of EDTA will be similar to their distribution in solution (cf. RFW), and they all can replace⁴⁷⁾ others when EDTA is present in excess amounts versus Fe(III) and Mg. Ca or Mn(II) are less tightly bound by EDTA. Speciation and photochemical transformations depend on these phenomena, too, with [Ni(edta)] even more reluctant to microbial processing in soils than the free ligand (Noertemann, 1999). “Occupa-

47) Although EDTA forms quite a number of (donor atom 1)-backbone-(donor atom 2)-Mⁿ⁺ rings during chelation, exchange is fast enough (it occurs within seconds) to

be relevant for environmental conditions. This fact was used in classical complexometry, with Mg²⁺ be replaced by Zn²⁺, the solution changing color thereby.

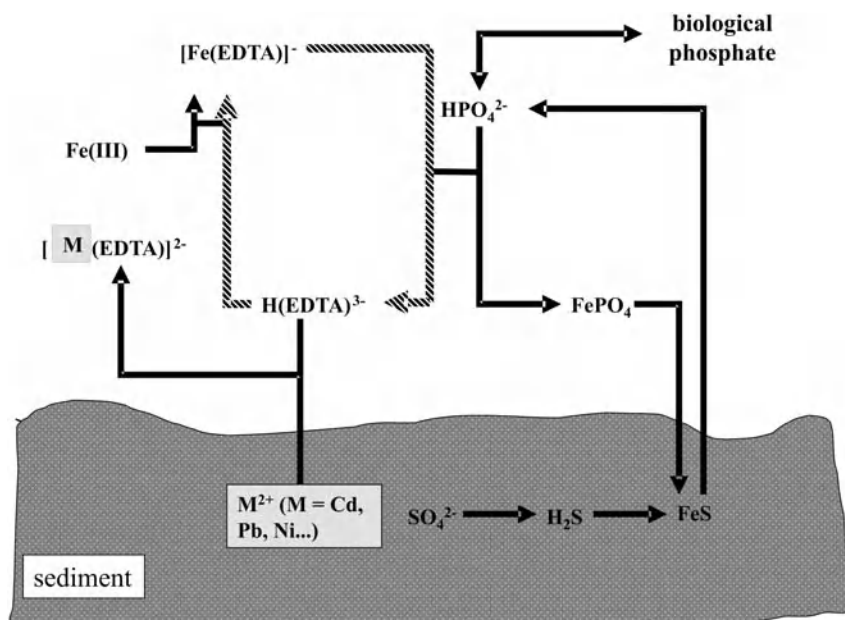


Figure 4.30 Being only reluctantly degraded by microbes, EDTA is about to mobilize toxic (and other) heavy metals from limnetic sediments. In a lake, there will be the following inputs which then interact via Fe(III) and other “common” reactants:

- 1) EDTA from various (though generally anthropogenic) sources;
- 2) Phosphate from fertilizers and human, animal excretions.

Further information in the text.

tion” of EDTA ligands by Fe(III), Mg and Ca can be released by adding phosphate which then causes precipitations of vivianite ($FePO_4 \cdot 8H_2O$) or some apatite variety, EDTA can re-start extracting toxic metals like Pb and Ni from the sediment. How long EDTA will last in the hydrosphere in these conditions, is controlled mainly by Mn levels [EDTA-manganese(III) complexes undergo photolysis much like Fe(III) or Cu(II) species]. If Mn is rare ($RFW \approx 10^{-7} M$), metal-induced photolysis is completely inhibited which in turn increases its persistence, hence EDTA equilibrium concentrations and in turn enhances possible extraction of Pb, Ni and so on from sediment once again. Figure 4.30 depicts this network of interactions.

The latter phosphate does cause precipitations of $FePO_4$, $AlPO_4$ or hydroxyapatite $Ca_5(PO_4)_3(OH)$ unless completely locked up in biomass (which will happen rather in oligotrophic conditions). In addition, more phosphate is released (recycled) from reducing sediment layers by converting $FePO_4$ into FeS_x [bottom right in Figure 4.30, given in black for color of iron sulfides rather than violet Fe(III) phosphate (here given in surrounded fields)]. Both interconnected cycles of phosphate and of EDTA, competing for Fe^{3+} , sensitively depend on levels of Fe(III) and Al(III) and thus of ambient pH. Only in eutrophic conditions, with substantial “free” (inorganic, not bound into biomass at present) HPO_4^{2-} and low levels of

Fe(III), Al, and alkaline earths (very “soft”, well-aerated water), there will be free EDTA, with the former ions being precipitated as the respective phosphates rather than forming EDTA complexes. Then, EDTA is left for extracting yet other metals from sediment, rendering them (more) bioavailable (short-cutting the black hatched cycle).

In less nutrient-laden freshwaters (Figure 4.30), most of phosphate is fixed by the biota, correspondingly reducing levels of dissolved inorganic phosphate and thus rates of FePO_4 precipitation. While and when phosphate sticks to biomass, Fe(III) and Al(III) will in turn stick to EDTA, blocking its extraction activity [stability constants of EDTA complexes of toxic divalent ions like Cu(II), Ni(II), Cd(II) or Pb(II) fall short by far of that of the Fe(III)-complex]. Only in N-limited growth, lack of nitrogen (nitrate) or else low water temperatures, limiting phytoplankton growth rates, substantial free phosphate will be there.

When Cu(II) is mobilized in this way also, growth of algae, phytoplankton is inhibited, further inhibiting biological fixation of phosphate. This causes some positive feedback. Conversely, if EDTA acts to extract scarce metal resources then open for plant nutrition, algal growth is enhanced. In these conditions, Fe will “occupy” EDTA until the algae start to die and sink down, making FePO_4 decompose in the sediment. Owing to persistence and photochemical inertness of free EDTA; it can be assumed constant in quite waters (in lakes, average levels are some 10 times higher than in rivers).

4.2.2.4 Principles of Action (Pathways of EDTA Degradation) and Technical Remediation: A Survey of Chances and Obstacles

Possible methods to get rid of EDTA include:

- 1) Microbial degradation in oxidizing (aerobic or even H_2O_2 -consuming) conditions;
- 2) Application of oxidant-reductant mixtures like in the FENTON reduction which produce aggressive radicals;
- 3) Photooxidation using (coordinated) metal ions;
- 4) Sonochemical decay by intense ultrasound, or (possibly):
- 5) Microbial decay in reducing conditions.

Option (1): microbial oxidation

Like with other strongly complexing chelators which “wrap” metal ions altogether, biological decay of free EDTA is strongly inhibited. In deodorant sticks, the capability of EDTA and similar agents even to extract metal ions such as Zn^{2+} from proteins which are essential for their function is used, stopping their functions in digestion (Zn-dependent hydrolyses, peptidases, etc.). However, EDTA can be degraded by oxidizing (respiring) microbes in the lab after converting into alkaline earth complexes. After successful degradation this metal addition must be removed in order to limit metal burdens in open waters. Yet, precipitation only takes place if chelators—both EDTA itself and its primary products—underwent complete mineralization.

Hence successful degradation will rather work along options (2–4).

Option (2): oxidizing mixtures which produces highly reactive radicals

Advanced oxidation procedures are quite a number of different although somewhat related procedures all of which aim at destruction (mineralization) of organic solutes like PAHs, amines, anilines, phenols (and other toxic ones such as CN^- , NCO^- , NO_2^- , etc.) by oxidation. Principal reagents are H_2O_2 , ozone and iron,⁴⁸⁾ combinations thereof and often near ultraviolet (NUV; $\lambda = 325\text{--}380\text{ nm}$) radiation which interact to produce OH radicals, ferryl(IV) ions or singlet oxygen. Similar reactions occur in drinking water preparation if oxidative sterilization by either ozone, chlorine or ClO_2 is done. However, apart from destroying bacteria and viruses, these latter processes fall short of complete mineralization, and the same happens upon chlorination of raw waters which contain dissolved EDTA or its complexes (cf. the above arguments on oxidative ligand exchange), producing some by-products which are severely toxic:

N- and C-centered chlorinations of amino acids including EDTA produce N-chloroamines (see below), NH_2Cl by their hydrolysis and chlorinated diketopiperazines which react further to produce chlorinated heterocycles of different kinds and ring sizes. Many of these compounds, among them some biogenic ones (Gribble, 2005), are highly toxic (e.g., occur in poison frogs) and capable of stopping microbial degradation of yet other compounds than EDTA by local microflora. This particularly holds for chloroamines. Some of these compounds⁴⁹⁾ even can kill larger aquatic organisms, including fish parasites. You have probably noticed the sequence of affairs in your local public indoor swimming pool (outdoors, both better venting and photochemistry relieve most of the nuisance): bathers release many N compounds, including amino acids (from the skin) and urea (source is obvious) which then all undergo chlorination unless water is purified by ozone rather than Cl_2 or ClO_2 . The typical “pool smell” is due to the chlorinated amines produced thereby, the most simple being NH_2Cl and NHCl_2 but also organic compounds (it is telling that similar smells arise when bleaching cellulose with trichloroamine NCl_3).

Concerning EDTA, hence the AOP method of choice avoided chlorine but took hydrogen peroxide instead. Since no metal ions were added and short-range UV was shined on the solution, the key intermediate was OH radical, allowing for EDTA degradation. Before there is complete mineralization, the (intermediate) product pattern differs from that seen with Fe(III) (Sørensen and Frimmel, 1995). Other oxidants were also studied, for example, using alkaline MnO_4^- solutions (Chang, Korshin and Ferguson, 2006) and do likewise remove EDTA entirely, with oxalate, formate and NH_3 being the principal, innocuous, products. In contrast, acidic permanganate oxidation stops at EDTra (Bose

48) “iron” for this purpose can be all Fe^{2+} plus an oxidant, Fe(III) activated by UV radiation, $\text{Fe}^{\text{IV}}\text{O}^{2+}$ (produced e.g., in Fenton’s reagent, and ferrate FeO_4^{2-}). Its advantage is that the residues of these usually cheap reagents are environmentally benign.

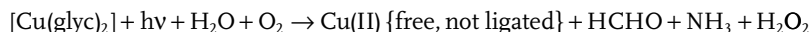
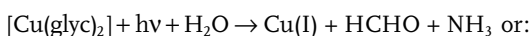
49) When breeding and rising fish in ponds, pisciculturists use “chloramine-T” (sodium salt of N-chloro-4-toluenesulfonamide) for this purpose. It is also sometimes used in oxidation titrations.

et al., 1991). The classical alkaline permanganate oxidation destroys a lot of organics and hence cannot be expected to be highly effective in solutions containing many other organics besides (maybe but small amounts of) EDTA.

Option (3): photooxidation employing metal ions

Unlike EDTA itself and many other amino acids (Dioses, 1988; Hill *et al.*, 1986), their respective complexes may be sensitive even to visible light (Horvath and Stevenson, 1992). Regardless of being a tertiary amino acid, EDTA shares the typical reaction features and pathways of amino acid complexes of numerous oxidizing (transition or rare earth elements) metal ions, including Cu(II), Fe(III), Mn(III), Co(III), Ir(IV), V(IV), Ce(IV), Eu(III) and so on:

MLCT photooxidation, which means the transfer of an electron from to the metal ion center, reducing the latter to yield Mn(II), Fe(II), Co(II), Ir(III) and the like, while the amino acid radical rapidly decomposes unless other reaction pathways are opened by additives or metal ions.⁵⁰ Here, decomposition is the objective of the procedure, the way of matters being explained in a most simple case, ligation and subsequent photooxidation of glycine by divalent copper:



Hydrogen peroxide formed in the given reaction can take part in additional photoreactions while Cu^{2+} released from the decomposed amino acid is now free to bind to yet other molecules—including other amino acids—thus activating them for photochemical transformation although the required wavelengths of some $230 \text{ nm} \leq \lambda \leq 300 \text{ nm}$ are at the shortest parts of the solar spectrum which makes it to the surface. In the corresponding iron(III) complex $[\text{Fe}^{\text{III}}(\text{EDTA})]^-$ iron also takes part in photocatalytic degradation of H_2O_2 (Lunak and Veprek-Siska, 1983) which can pose problems in actually running AOP methods for EDTA cleavage which depend on H_2O_2 providing OH radicals (or, particularly photoassisted, the FENTON reaction).

Concerning EDTA complexes, photooxidation (Figure 4.31) is fastest (highest quantum yield Φ) when combined with Fe(III) while those of trivalent Co and

50) For subsequent reactions, see Poznyak and Pavlovski (1988): loss of CO_2 leaves behind a reactive aminoalkyl radical which is still next to the metal center. Apart from further reducing it to become an immonium ion then liable to hydrolysis giving ammonia and aldehyde, it can react with the metal itself (most so with Co, Rh, Ir, Pt) to form a three-membered M-C-N ring (Poznyak and Pavlovski 1988). Another pathway is realized (Fränzle *et al.*, 2010) by adding a semiconductor having a sufficiently large and well-positioned band

gap to the photolyzing amino acid-metal complex solution: then $\text{R}_2\text{N-CH}_2\text{-COO}^\bullet$ regains an electron fast enough by hole injection to avoid decarboxylation. Actually the NC_2O backbone of glycinate remains intact even when some part of the ligand reacts with oxidation intermediates of other organics which undergo photocatalytic oxidation from their adsorbed states. Here, a C_2H_4 unit is transferred to glycinate, making morpholinone (Fränzle *et al.*, 2010).

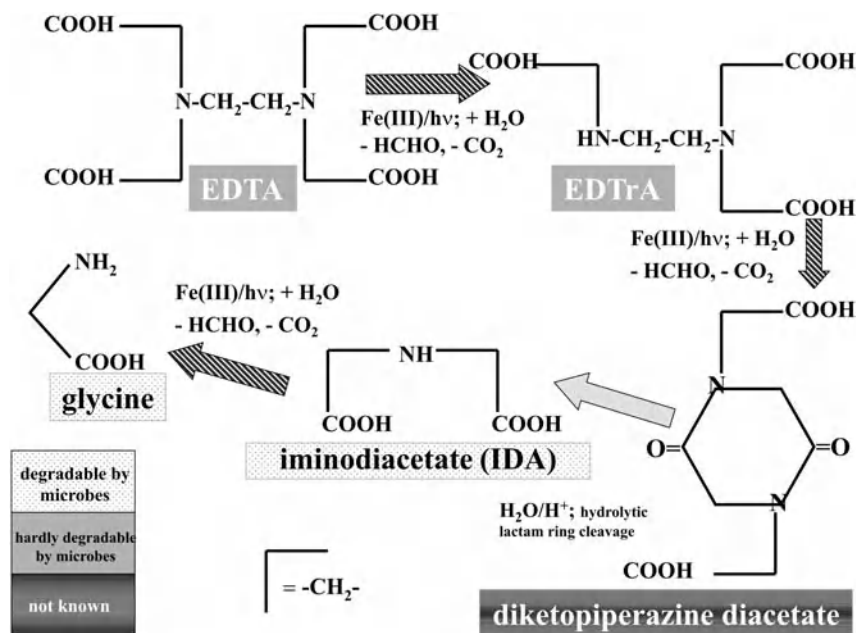


Figure 4.31 Photochemical degradation pathway of EDTA linked to Fe^{3+} (Fränzle, Markert and Wünschmann, 2005). Different grays are used to distinguish biodegradable later stages of decomposition (which in addition form weaker complexes) from educt EDTA and primary product EDTrA which resist microbial attack. Dark shaded arrows

denote the photoprocesses induced by $\text{Fe}(\text{III})$ coordination while the light shaded arrow symbolizes diketopiperazine diacetate (DKPDA) undergoing hydrolytic lactam ring cleavage to yield iminodiacetate IDA. For mechanistic details of the first step of EDTA degradation, see Kocot, Karocki and Stasicka (2006).

Mn take place some 10–20 times slower (European Chemical Industry Council; CEFIC, 2003). Other metal complexes of EDTA significant for the environment are reported⁵¹⁾ not to undergo LMCT photodegradation cleaving N atoms and terminal C_2 units. The ligand anion in the LMCT state (by definition) is taken off an electron; here—like with both proteinogenic or yet other amino acids or hydroxiacids or simple carboxylatoligands like oxalate, malonate, propanoate (Grikos and Hennig, 1988)—loss of carbon dioxide from the ligand radical $\text{R}_2\text{N}-\text{CH}_2-\text{COO}\cdot$ is rather fast (nano- to at most microseconds). The secondary radical $\text{R}_2\text{N}-\text{CH}_2\cdot$ with an ionization potential of $\ll 6\text{ eV}$ (the lowest among the metal-free neutral radicals) is a very powerful 1e-reductant (cf. Jonsson *et al.*, 1999) with an estimated potential much below -1 V , hence rapidly reducing the educt complex (if it can bind another electron), dissolved oxygen or other acceptors, like quinone moieties in humic acids. The next (reversible) step is

51) Omitting the ultratrace components of fresh water, EDTA complexes of $\text{Cu}(\text{II})$ and $\text{Ce}(\text{IV})$ should yet react. For $\text{Cu}(\text{II})$, only the shortest parts of UV radiation which make it to the surface are active but with $\text{Ce}(\text{IV})$, matters are different.

hydrolysis of the $(R_2N-CH_2)^+$ cation thus formed; here HCHO is released to produce another amino acid which has been “restricted” by one acetate function, that is, primarily ethylene diamine triacetate EDTrA. Then a ring is closed by intramolecular lactam condensation to afford diketopiperazine⁵²⁾ diacetate DKPDA. Although many diketopiperazines and other cyclic oligopeptides are highly active in both physiological and pharmaceutical meanings of this term, diketopiperazine diacetate does not harm any of the common test organisms up to levels of $>100\text{ mg/l}$, that is, more than 30 times the maximum EDTA concentrations seen in industrial effluents. As simpler amino acids and lactams are both capable still to undergo these photochemical transformations [provided their complexes are sufficiently stable to maintain metal ion (Fe) binding at ambient Fe, etc., concentrations], degradation goes on now to cleave the ethylene bridge which hitherto linked the two N atoms. Then iminodiacetate and glycine arise both of which are susceptible to attack by living organisms.

Hence it is actually feasible to get rid of the properties of EDTA and EDTrA which cause the ecotoxicological problems associated with these substances (and with NTA, DTPA, cyclohexane oligo-aminodiacetates, etc.).

As discussed above, EDTA complexes of transition metals and rare earth elements are so stable that the common levels of EDTA in, for example, German rivers of some $30\text{ }\mu\text{g/l}$ (100 nM/kg) will safely bind these ions into EDTA complexes [there are hardly any natural ligands other than humic acids and siderophores (hydroxamates, polyphenols, salicylates) which can compete with these complex stabilities to preclude prevailing formation of EDTA complexes]. After their being reoxidized by oxygen or nitrate both stability and photoactivity of the complexes do increase. A photocatalytic cycle (Figure 4.32) will thus arrange provided there are reasonable levels of appropriate metal ions while O_2 is available.

Option (4): sonochemical degradation

As cavitation bubbles absorb only neutral species, EDTA sonochemistry is gravely influenced by its being a rather strong acid ($pK_{a1} = 2.00$; $pK_{a2} = 2.69$; $pK_{a3} = 6.13$; $pK_{a4} = 10.1$; Mizerski, 1997). In fresh water ($pH = 5.0\text{--}8.5$), di- and trianions of EDTA will thus prevail, keeping it from ever getting into cavitation bubbles. Hence it will not feel the heat and pressure generated there by acoustic cavitation to destroy these or other organic molecules and even activate N_2 . Nevertheless, there are reports on sonochemical degradation of EDTA to afford glycine and more complicated chelating molecules. Hence, probably the

- 52) Diketopiperazines are the most simple possible peptides, connecting two amino acids not just by one carboxamide moiety but by (all) two, closing the peptide to form a six-membered ring. The carboxamide linkages formed here are completely identical to peptide bonds on

open-chain peptides. Moreover, cyclic oligo- and polypeptides are also produced by many living beings, the most known (and notorious) being perhaps the amanitines, two double-ring decapeptides produced by death cap fungus *Amanita phalloides*.

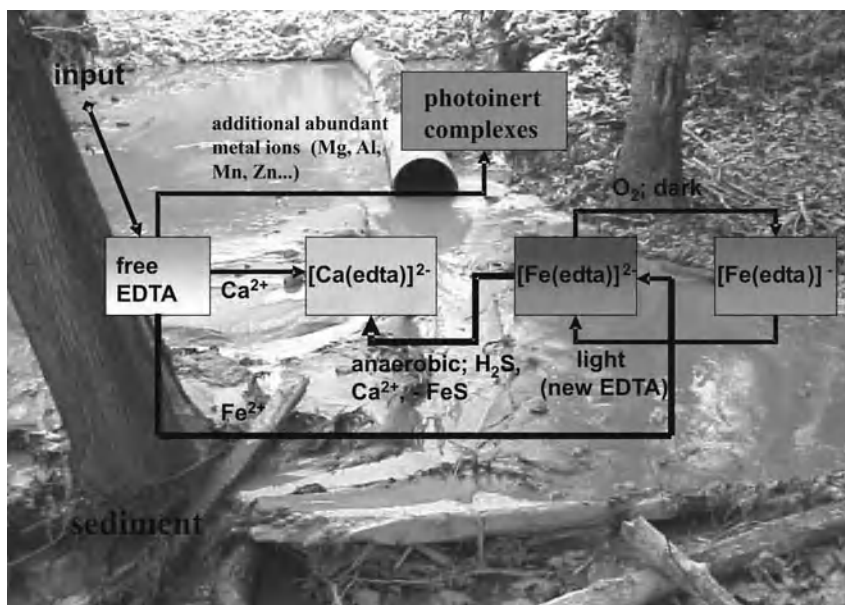


Figure 4.32 How photochemical transformations, EDTA “loading” by metal ions Mg, Ca, Al, Mn, Zn and redox processes (by Fe) interact in EDTA mobilization of heavy (and some other) metals from wet or inundated sediments. As described above, it takes soft water and certain other conditions to get metals actually mobilized. EDTA getting into open water as a free ligand will react with many different metal ions to yield complexes. Which ones are obtained depends on both the freshwater composition, redox potential and UV flux rate*: if there is sulfate reduction in water-logged soils or meromictic water bodies, Fe and most other metal ions will be precipitated as sulfides, leaving $[\text{Ca}(\text{edta})]^{2-}$ as the most stable species which can be produced with a still abundant metal ion (sulfate reduction is possible in regions which still are photic, giving S^{2-} -oxidizing photobacteria a chance to obtain electrons for CO_2

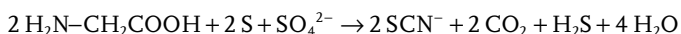
reduction other than from oxidizing water). Nevertheless, $[\text{Ca}(\text{edta})]^{2-}$ is also kinetically much more labile than either iron complex of EDTA, allowing the extraction of heavy metals which are unable to form very stable sulfides (Mn, rare earth elements) from the sediment. In oxic conditions, however, EDTA complexes of Fe(III) and other ions like Cu(II) form which are much more stable than those of Cd, Pb. Hence, in oxidizing conditions no toxic heavy metals other than Hg may be mobilized, except with strong UV irradiation. In tropical blackwater biotopes, humic acids do not succeed in efficiently leaching and transporting metals, thus EDTA would demetallate humics almost completely (see text). Yet, Hg^{2+} could be mobilized by EDTA as its complex is about as stable as $[\text{Fe}^{\text{III}}(\text{edta})]^{-}$. Background photograph courtesy of: www.state.me.us; scheme overlaid by the authors.

* Photoreduction of Fe(III) by, for example, humic acids is so efficient under ambient UV radiation, that during the daytime most of the iron is Fe^{2+} , even in shallow, strongly aerated waters like mountain creeks.

experiments were not done in distilled water but involved neutral, that is, uncharged metal complexes formed between EDTA and Mg^{2+} , Ca^{2+} , Al^{3+} . Given actual tasks in environmental technology, this is not a drawback but a more realistic representation of ambient conditions. Sonochemical activation of sulfide sludges (with or without parallel shining UV radiation on them) for heavy metal extraction was also demonstrated.

Option (5): microbial degradation in reducing (anaerobic) conditions

There apparently is no reductive cleavage of EDTA or similar synthetic amino acids which could be compared to the action of glycine phosphoreductase in, for example, clostridia (a Fe/W/Se enzyme); no EDTA degradation can be detected in anoxic soil layers. In terms of thermodynamics, an oxidation of acetate side chains or the entire backbone using sulfate as a terminal electron acceptor according to, for example:



would be possible but an hydride transfer here also is excluded by the branched structure of the tertiary amines.

With reductive microbial processes bound to fail, there is only the chance to run aerobic (or using even stronger oxidants than O_2) processes, including the photo- and sonochemical methods. The photochemical methods also need aerobic conditions, because the metal ions must be re-oxidized by air or something else to further promote photooxidations, that is, to be employed as catalytic agents in mineralization of organics. Experiences from sewage water treatment plants have it that nonbiological methods of removing certain classes of pollutants are superior to attempts of biodegradation, with “classical” AOPs being less effective than the various [homogeneous, heterogeneous (photoelectrochemistry), supported LMCT] procedures. Highly polluted wastewaters, including residues of cellulose production or of (now phasing out) photographic developer liquids are probably more difficult to treat by photochemical means, giving a larger role for direct oxidation and/or sonochemistry. Oxidizing conditions are mandatory throughout the processes, photochemical ones need an addition of Fe^{3+} while biological treatments call for Mg^{2+} amendments.

4.2.2.5 Practical Experience

With metal ions like Fe(III) present, photooxidation occurs in a way of stepwise cleavage of single acetate sidechains. This converts the hexadentate EDTA which accordingly produces much more stable complexes than one-, di- or tridentate ligands, into a series of “poorer” ligands, with any next one being less able to bind traces of metal ions than the antecessors. Hence metal ion-induced photodegradation may stop, namely, if complexes become unstable in environmental conditions. In addition, secondary ligands produced in the series of photochemical events, for example, IDA, glycine or oxalic acid, become more liable to biological absorption and metabolism, once more reducing their average (flow equilibrium) concentrations. Metal-free photodegradation is not compromised by these effects,

first cutting in half the ethylene bridge but it only occurs at wavelengths much below the tropospheric threshold, hence lamps are required.

Except for one, the products of Fenton or photo-Fenton oxidations are not yet pinpointed (identified) but are assumed to be unable to further chelate metal ions, which means their complex formation constants are unlikely to be larger than that of glycinate. Oxidation by H_2O_2 with co-application of 254 nm UV radiation does not afford toxic products (Sørensen and Frimmel, 1995), which is in some contrast with the list of products given by the same authors which combines “actually” harmless compounds/ions like iminodiacetate, glycinate, oxamidate, oxalate or formate and inorganic CO_2 , NH_3 and NO_3^- with more troublesome ones like glyoxylate, nitrite and cyanate OCN^- . The quantum yield is reported to be high, making the reaction fast.

Products of ultrasound treatment (at either 40 or 130 kHz sonication frequencies) are not known precisely either but likewise reported to be efficient (chelating) ligands no longer. Additionally, COD (chemical oxygen demand) is reduced by sonolysis, suggesting an oxidation of the EDTA molecule backbone to happen which entails cutting away the amino acid moieties.

4.2.2.6 Conclusion

Waste waters polluted by EDTA inevitably require particular chemical–technical secondary treatment beyond classical sewage water processing. The problem of biochemical attack being most difficult is relieved by using either photochemical protocols or other processes which afford OH radicals. While Fe(III)-promoted photooxidation will occur at limited rates under ambient conditions, turnover can be considerably increased in a cleaning device. This very behavior is likewise observed in photooxidative degradations of other organics which behave as ligands.

EDTA, NTA, DTPA are but a few among a considerable number of organics the complex-formation propensity of which considerably influences their possible degradation pathways. Besides DTPA, some (rare earth elements) complexes of which are employed in medical diagnostics,⁵³⁾ one critical case is the broad-spectrum herbicide glyphosate⁵⁴⁾ (Roundup™). Persistence issues are similar while glyphosate, moreover, is toxic to vertebrates also. Neither ligand can be decomposed in sewage treatment plants to an appreciable extent. While photochemical degradation is simple and straightforward in the laboratory, the extremely slight solubility of vivianite requires phosphate to be absent from the waters to be treated—and this would be fairly strange considering the composition and origins of colloquial communal wastewaters. If one tried to overcome this solubility drawback by replacing Fe(III) with some other photoactivating metal ion, this probably

53) Being an octadentate ligand, DTPA is best in binding such metal ions which prefer coordination numbers larger than six, like rare earth elements. Among these, a Gd(III) DTPA complex is used for contrast in MR tomography. It is renally excreted after being supplied to the patient intravenously. After this Gd(III) DTPA

complex Gd levels in communal wastewaters—in general, not just those of clinical institutions—increased considerably, with the complex persisting in sewage waters as is (Kümmerer and Helmers, 2000).

54) N-methanephosphonatoglycinate.

would imply either removing or withholding it from the effluent afterwards by additional measures.

4.3

Water

4.3.1

Reactive Walls

4.3.1.1 The Problem

After getting into soil from either the surface or underground structures, dissolved inorganic (e.g., “heavy metals”, cyanides) and organic pollutants (halogenated, biocides of most diverse structures, nitrocompounds, crude oil hydrocarbons) undergo transport by groundwater. These pollutants may be derived from agriculture, mining, abandoned industrial sites, accidents during the transport of fuels and other chemicals or from geochemical processes. This puts hazards on all drinking (potable) water—most of which is derived from groundwater, often employing riverside ground filtration—and on the living beings in open waters and eventually the birds, humans and others consuming these aquatic creatures. There are various methods to clean up groundwater polluted in such ways; one of them being *pump and treat*: collect and pump up water in some well, clean it, for example, by adsorption and then pass it back into the ground. This approach meets at least two kinds of difficulties:

- 1) If large amounts of water are removed by the wells constructed for this purpose (in order to achieve clean-up within reasonably short periods of time), cracks and sink-downs will form in the soil body. Even without heave accidents [bearing capacity failures, e.g., like the one which destroyed the city archive in Cologne, Germany, by collapse of the entire building (and those around) above and into a new subway line (two young men killed, damage >1 bio. €) in 2009], the stability of buildings above and around such sites is compromised by these cracks. In addition they provide new ways along which polluted groundwater can flow to escape cleaning within a constricted part of the volume.
- 2) It is impossible to use this method for treating really large groundwater volumes like the 200-mio.-m³ groundwater bubble almost saturated by chlorobenzene and chlorinated naphthalenes at Bitterfeld (Saxony-Anhalt, former German Democratic Republic; GDR).

Reactive walls now (since the early 1990s) are an alternative to temporarily removing the waters from the site (i.e., *ex situ* procedures), being barriers permeable for water which are placed perpendicularly to the (free or funneled) groundwater flows (cf. Figure 4.33). This can be accomplished in different ways, by:

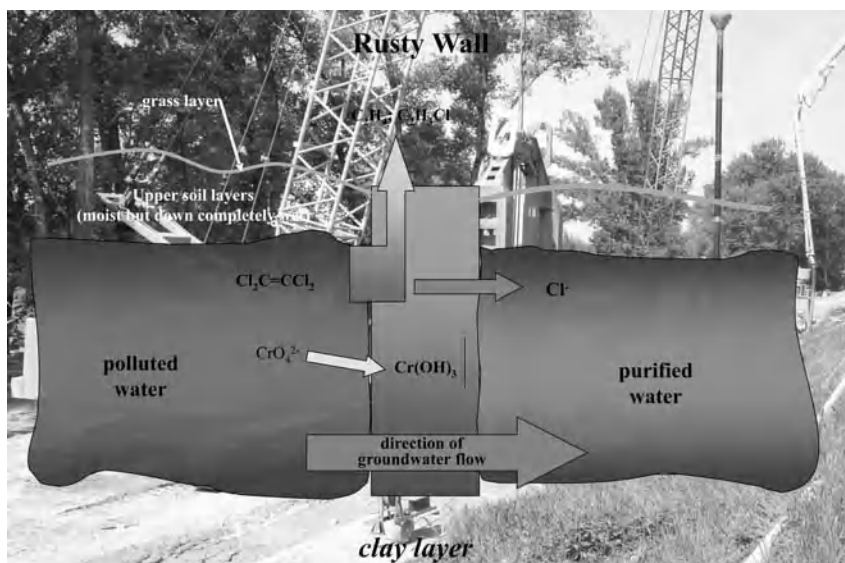


Figure 4.33 This sketch refers to a mixed organic and organic soil contamination which—both in general and with respect to this specific composition—is typical of metal processing enterprises such as galvanic plating factories. Here, chromate and organics like perchloroethylene (C_2Cl_4) are combined. Polluted groundwater (left side) is waiting to be moved to the reactive barrier (either passively or by pumping on the other side) whereas the right side symbolizes the cleaned water obtained by passing it through this barrier. Unlike liquid perchloroethylene, dehalogenation products C_2H_4 and C_2H_3Cl are gases and hardly soluble in water which hence escape upward to the atmosphere from the reactive wall. As a byproduct of CHC

reduction by Fe metal, chloride ions are produced which are dissolved and taken with the purified groundwater flow off the reactive barrier. The reactive wall produces alkali ($pH \approx 11$); hence CrO_4^{2-} is not only reduced into trivalent chromium but is then precipitated as hydroxide $Cr(OH)_3$. Thus, the hydroxide will be precipitated right inside the “wall” region which accordingly behaves like an actual rather than porous barrier (vertical black line). The drawing is not to any scale but it is mandatory that the reactive wall is constructed from the surface right down beneath the lower limit of the aquifer to be purified. Otherwise, the polluted water would flow somewhere round without being purified. Scheme overlaid by the authors.

- Digging trenches from the surface down to the lower edge of the polluted aquifer (this edge defined by clay layers, bedrock, lignite etc.);
- Pressing a reactant mixture into the soil to produce some confined “curtain” covering the same area;
- Producing drainage channels filled by the reactant so that the water must pass through it to go further downstream.

Materials providing a reactive barrier should be fairly stable toward water but (in the best cases) react with all the pertinent pollutants, immobilizing or removing them.

4.3.1.2 Principles of Action and Practical Solutions

There are three different modes of action which operate in a reactive wall:

- 1) Metal ions having a rather high reduction potential (i.e., “noble” or “semi-noble” ones) are deposited as pure metals (cementation).
- 2) An alkaline pH is produced spontaneously in the reaction zone, causing also many metals which are redox-inert, such as rare earth elements, to be precipitated as either hydrated oxides or hydroxides.
- 3) From organic compounds, halogens are cleaved by reduction whereas nitro- and some other functional groups undergo hydrogenation.

1) Cementation

Cementation is a redox process which occurs on the surface (aqueous interface) of some reactive (base) metal like iron or zinc. Then, metals ions (Fe^{2+} or Zn^{2+} , respectively) are leached from the metal–liquid interface while more “noble” metals (Cu, Ag, Bi, Au, PGM) are precipitated from surrounding solutions, forming metal surface films, in some cases outright mirrors (Ag, Hg). This is a spontaneous process: an iron key immersed in a Cu^{2+} solution soon becomes covered with copper!⁵⁵⁾ Figure 4.34 shows: (a) “fresh” iron filing (cleaned before by rinsing with acetone) and (b) (to the right) Fe filings which got covered by copper metal by immersion into a dilute Cu^{2+} solution; that is cementation. Other than the reduction of chromate at an aqueous Fe surface, this reaction is almost complete within one minute even at pH 7. In the beginning, before adding iron filings, the CuSO_4 solution is blue, of course (Figure 4.34a), then to become almost completely decolorized (Figure 4.34b) as the product solution of FeSO_4 is but slightly greenish. In Figure 4.34c there are shown iron filings after cleaning (left) and after being covered with cementated copper (right).

Of course, each of the three principal kinds of reactions will take place only if they are feasible in thermodynamic terms. That is, the reactant constituting the active part of a reactive wall—there are pretty different setups of these devices—must be sufficiently reducing not only to accomplish the reaction “theoretically” but also to overcome the (often substantially large) activation barriers, called overvoltages in the case of electrochemical transformations. But it is not wise to employ too strong a reductant, like aluminum, since:

- Then hydrogen gas will be produced which is going to escape to the atmosphere unless there are catalytically active metal surfaces like nickel or

55) The reverse coverage of rather noble metals by more reactive ones (Zn or Cd on steel, chromination of Cu pipes), conversely, takes an external source of energy, must be enforced either by electrochemical methods (cathodic plating),

by condensing metal vapors on the surface (fire plating by zinc or cadmium) or simply by immersion into corresponding metal melt baths. Anyway, this will not be a spontaneous process.

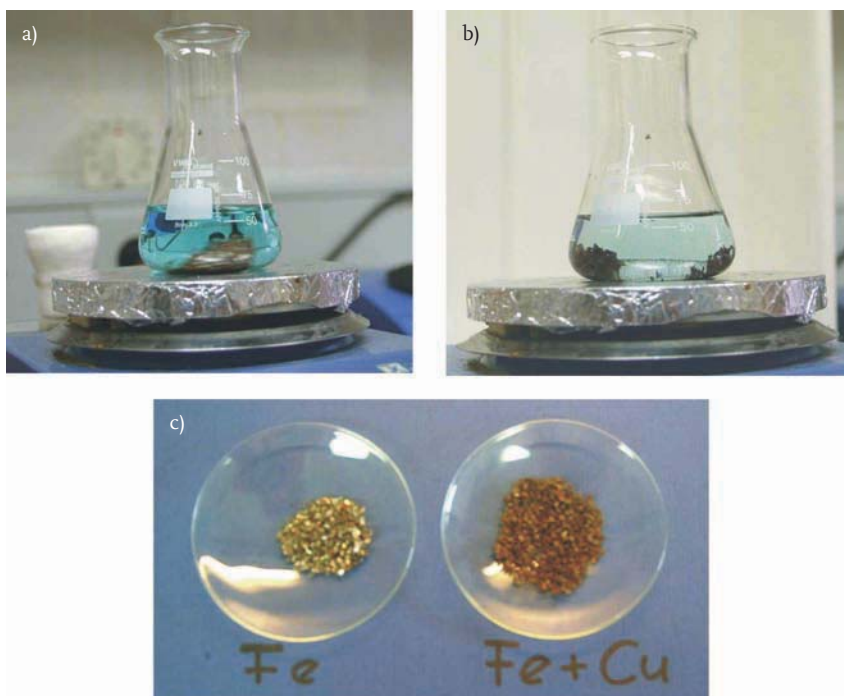


Figure 4.34 Copper gets deposited spontaneously (cementation) on iron metal filings, arranged along the magnetic field lines of the white stirring bar at bottom in (a, b). The time lag between (a), photo taken immediately after reagents were mixed, and (b) is some 90 s. (c) Iron filings just after cleaning and after being covered with copper cementation. Photos from Fränzle, Markert and Wünschmann (2005).

platinum group metals, not to mention ignition and explosion hazards associated with this.

- Strong reductants will drive reductions of elements like arsenic beyond the optimal (least soluble, least toxic) state.

Apart from this, matter conservation holds which means that neither metals like Fe nor organic reductants are going to “vanish” but they will leave behind metal cations or oxidized organic matter. For the procedure to be safe and meaningful, it is mandatory that these by-products of pollutant reduction be neither seriously toxic themselves nor cause too grave effects on soil chemistry. Taken together, these criteria combine to provide severe limits on materials a reactive wall may be made from. As might be anticipated, the three kinds of reactions mentioned above differ concerning the required potential, when both cementation or precipitation of some reduced form (insoluble binary or mixed aquoxide/hydroxide) pose different demands according to the substance which shall be “inactivated”; the same holds for the reduction/dehalogenation of toxic organics. Corresponding values—just meant to give

Table 4.4 Selections of redox potentials (or half-wave polarographic potentials) of different chemical systems at pH = 0 and 11, respectively.

Redox couple	Standard potential versus NHE, (normal hydrogen electrode) pH = 0	pH 11 redox potential (corresp. to Fe reactive wall conditions)
Fe/Fe ²⁺	0.45	0.5
H ₂ S/SO ₄ ²⁻ (compost wall)	0.30	-0.35
PhCl/PhH + Cl ⁻	1.04 (calculated)	0.39
Nitrobenzene/aniline	1.22 (calculated)	0.57
Cd/Cd ²⁺	-0.40	Ca. -0.6
Cd ²⁺ + SO ₄ ²⁻ /CdS (compost wall)	1.06 (calculated)	
HCrO ₄ ⁻ /Cr(OH) ₃	1.35	0.17
HAsO ₄ ²⁻ /As	0.37	-0.46
As/AsH ₃ (unwanted reaction)	-0.61	-1.26

an idea of what is required or to be avoided—are given in Table 4.4, considering the two principal practical forms of reactive walls, namely using either iron (scrap, usually containing a few percent of Ni) or compost. Either kind of wall permits a reduction of chromate to afford Cr(III) or both arsenite and arsenate(V) to produce neat arsenic, likewise nitrobenzene will be converted into aniline⁵⁶⁾ and chlorobenzenes into benzene while production of arsane AsH₃ fails for thermodynamic reasons.

Because reactive walls can be pretty large constructions, filtering groundwater over cross-sections of hectares in certain cases, materials in such a wall must also be affordable besides having low toxicity (if any) and a “suitable” redox potential. Notwithstanding this, Mg, Al, or Zn which command a few \$/kg could readily replace Fe which, of course, is even cheaper when taken from scrap. When compost (which itself, notably, is prepared in aerobic conditions!), sawdust, straw and similar organic samples are used in reactive walls rather than any metals, you end up with an organic reactive wall which works by sulfate reduction mainly, with H₂S formed in it both precipitating (heavy) metal ions and cleaving aliphatic as well as aromatic halogenated hydrocarbons. There is some serious reason to yet avoid using the above cheap, hardly toxic metals Mg, Al or Zn: they are *too* powerful as reductants. If arsenic gets into contact with zinc, magnesium or aluminum, the product will be arsane AsH₃, which, unlike elemental As, is a gas and thus vented from the reactive wall along H₂. There were intoxication accidents—including fatal ones—when As-containing groundwater made its way into wells having claddings made from aluminum. That AsH₃ may be formed can be deduced from the Pourbaix

56) At T ≈ 10 °C, low nitrobenzene concentrations and high pH (about 11), otherwise an iron reduction of nitrobenzene yields azobenzene Ph-N=N-Ph.

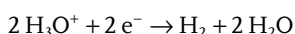
diagram of As versus Al; this also holds for Zn (Marsh's test!⁵⁷⁾) and, of course, for all the stronger reductants including magnesium. Notably, As reduction often goes beyond neat arsenic in the terrestrial pedos- and lithosphere also: some bacteria (clostridia and others) may produce AsH₃ and organoarsenic hydrides (Thayer, 1995; Cheng and Focht, 1979), and there are arsenide minerals probably produced by (biochemical?) precipitations of Cu or/and Ag salts. Corresponding standard potentials (Al -1.70 V, Zn -0.76, Mg -2.36 V) are way below that required to reduce As compounds into AsH₃.

Figure 4.35 thus is meant to illustrate some of the side-reactions which give rise to often highly toxic by-products, whereas reduction of haloaromatics and cementation (or sulfide precipitation, respectively) could be done with all the varieties of reactive walls discussed above. Besides arsane and similarly toxic stibane SbH₃, metal carbonyls and alkyl compounds such as lead tetramethyl may also form (Ahmad *et al.*, 1980). If organobromine or organoiodine compounds are present, Al metal will attack lead (!) in alkaline conditions to form highly toxic (neurotoxic) lead alkyls which once again are volatile and lipophilic, hence accumulating in man and animals. Hence it is wise to refrain to iron metal or else sulfide-forming organic barrier materials, each kept together by geotextile wrappings. The latter sulfide precursors also can process halogenated aliphatics including CCl₄.

Now have a look at the two other principles of action encountered in a reactive wall.

2) Alkaline hydroxide/aquoxide precipitation induced by action of reductants

If electrons are passed into an aqueous system (the same holds for other protic solvents), the pH value of the solution tends to increase; in the most simple case the autoprotolytic equilibrium is shifted to more hydroxide by reducing oxonium (or more generally: solvent acidium) ions into H₂ + solvent, namely:



But there is yet another reason for this pH increase, which is also made use of when "deacidifying" lakes prone with sulfuric acid by enforcing biochemical sulfate reduction: both the acidities of non-metal

57) Marsh's test, developed back in 1836, was used in forensic medicine in earlier times to detect traces of arsenic in biological samples (stomach content, organs of bodies, food). Besides also detecting even more toxic antimony, which likewise was often abused for homicide during the nineteenth century (Emsley, 2005), Marsh's test also works with most organoarsenic compounds (some of which were CW agents) and residues of Ge, Se, most toxic

(Diaz-Bone *et al.*, 2011) Te and their respective organoelement compounds. The method relies upon the formation of binary hydrides or R_xEH_{n-x} compounds (n = 1–4, 3 with As and Sb; x = 0 – 3) by zinc/HCl_{aq}. The hydrides thus formed are either thermally decomposed to produce some "mirror" of element-specific chemical properties or put to AAS (element identification only) or GC/MS (this also allowing for speciation analysis).

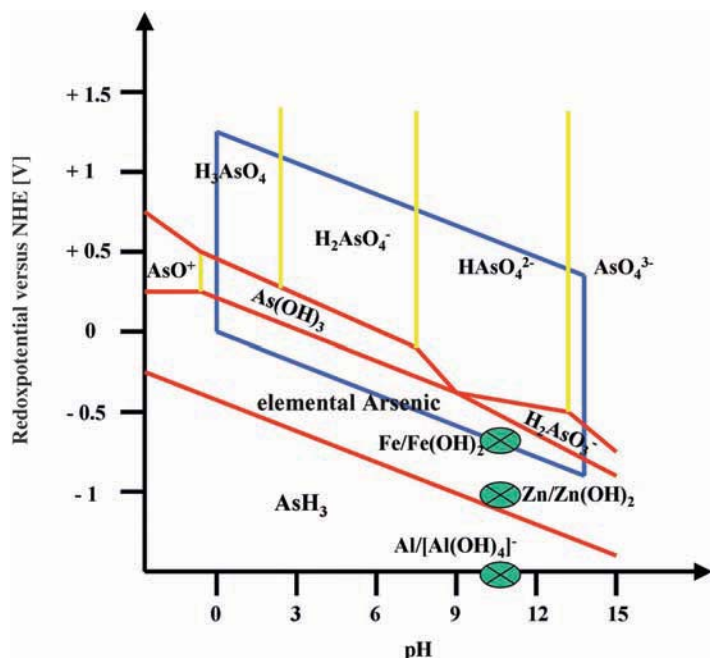


Figure 4.35 Because activation barriers are small, oxoanions of quite different elements can be possibly introduced into soil liquid as contaminants (including oxoanions of arsenic, chromium, or technetium). Around 1950, it was commonplace practice simply to spill fission product mixtures, containing lots of Tc, onto the ground after separating U, Pu and some valuable components in both the United States (Hanford, Wash.) and the then USSR. Speciation of As mainly occurs according to the Pourbaix diagram (superpositions) as overvoltages tend to be small. For example, when groundwater gets into contact with reactive walls or well claddings, hours to weeks are available for the reaction, getting even closer to equilibrium states. Green dots show elements (metals) which might be introduced into some reactive wall (considering only toxicity and price), namely Fe, Zn, Al and their respective redox potentials. When such reductants are there, the surroundings of the reactive wall will spontaneously adjust to a pH of about 11 which corresponds to the

position of the dots in the diagram. While iron can reduce arsenic compounds only into neat As [with the redox couple $\text{Fe}/\text{Fe}(\text{OH})_2$ located inside the stability region of the latter],* Al will promote reduction to the ultimate point of arsane AsH_3 , while both redox potential and product distribution by zinc will be “in between.” While, unlike in acidic solutions (Marsh’s test), reduction will not afford 100% of AsH_3 , it still occurs to some extent which needs to be considered, given the extreme toxicity of arsane. Moreover, both Zn and Al can also reduce products of biomethylation and classical biocides like (Na) methyl arsonate into primary (here: $\text{CH}_3\text{—AsH}_2$) or secondary arsanes which, like AsH_3 , are both most toxic and highly volatile. With arsane and its simple alkyl derivatives being much more toxic than both neat arsenic and even As(III), Zn, Al, or other similarly reducing metals (Mn, Mg, V, Ti) must be kept from contact with groundwater when arsenic is present, be it for geogenic reasons or owing to contamination.

* Of course, similar considerations hold for redox potentials and products of non-metal couples brought into contact with oxidized forms of arsenic, for example, the alkaline CN^-/NCO^- couple (producing neat As,

Berzelius’s test for arsenic, producing a brownish colloid selectively) or $\text{SO}_3^{2-}/\text{SO}_4^{2-}$ (same result, but less specific) (cp. Jander and Blasius, 1978).

oxoacids⁵⁸⁾ and of aquated metal cations increase with increasing formal oxidation state. Bell's rule does put this into numbers: when there is an additional oxygen atom introduced into an oxoacid, increasing the oxidation state of the central ion, pKa will decrease by five to six units, causing a severe increase in acidity. An oxoacid or aquaion of a reducible metal which undergoes reduction next to or inside a reactive wall will lose most of its acidities toward soil liquids. In polluted soils, typical acids of either kind include nitric acid, $\text{Cr}_2\text{O}_7^{2-}$ (hydrolyzing into HCrO_4^-) and Fe^{3+} . Another less obvious feature of this increasing alkalinity is due to the capability of a reactive wall also to "treat" halogenated or nitrocompounds, being all of substituted carboxylic acids, phenols and nitroalkanes: phenol is much less acidic than pentachlorophenol, acetic acid less so than chloroacetic acid (pKa = 4.75 and 2.81, respectively), nitromethane which is an acid even in water (pKa = 10.2; Mizerski, 1997) turns into formaldoxime or even methyl amine bases. The actual pH of about 11 thus is determined by the exact kinds and extents (product concentrations) of both the reactive wall and the reactants directly around. There are different implications of this:

- Most metals become precipitated at about pH 11 as hydroxides or aquoxides even unless undergoing cementation.
- There is a profound change in reaction kinetics. For example, chromate will hardly react at pH 7 with iron filings—even if these were cleaned and degreased before—and in acidic media reduction only takes place when there is vigorous dissolution of iron-producing Fe^{2+} ions and H_2 , yet at pH 11 reaction will be almost quantitative within a few hours at room temperature. Retention of chromium after chromate spills into soil solutions is one of the main fields for application of reactive walls.

Unlike the light metals considered as alternatives in reactive walls above (Zn, Al), iron is stable toward alkaline corrosion, being protected by an insoluble aquoxide layer while Zn or Al dissolution goes on by dissolving and carrying away hydroxometallate $[\text{M}(\text{OH})_4]^{x-}$ ions ($\text{M} = \text{Zn}$, $x = 2$; $\text{M} = \text{Al}$, $x = 1$). Hence

58) For example, consider the following pKa values conforming to Bell's rule: HOCl 7.53; HClO_2 1.95; HClO_3 -2.7; HClO_4 ca. -9.5, also HSO_3^- 7.18; HSO_4^- 1.99; also H_3AsO_3 9.29; H_3AsO_4 2.24 (Mizerski, 1997). With aquaions of metals which use to differ by one rather than two oxidation states from each other, the effects are still more pronounced: Fe(II) pKa = 9.4, Fe(III) 2.18, V(II) 6.5, V(III) 2.3; Cr(II) 8.2, Cr(III) = 4.26, Cr(VI) < 0 [strong acid, dissociation superposed by condensation into oligochromates(VI)]. Since a reduction of non-metal oxo acids by two (or six or eight) oxidation states does not necessarily correspond to an equal oxidation of metal,

the effects will not cancel; hence the above-mentioned pH of about 11 along a rusty wall will be reached even in soils that had been deliberately polluted with nitric acid.

59) Other metals which dissolve or form stable basic complexes (amphoteric behavior) actually display autocatalysis in their oxidative dissolution, bringing about all the remarkable features of non-linear chemistry: patterns and reaction fronts form on corroding metal interfaces (e.g., with cobalt or chromium), or an "explosion" into an uncontrolled, violent reaction (when K, Rb, or even Cs are contacted with liquid water or "warm" ice).

reductions at an iron interface are not autocatalytic⁵⁹⁾ but occur with well-defined and constant kinetics. Metals which do not undergo cementation for being more reducing than iron itself, like Al, keep dissolved in an alkaline environment created by the very reactive wall not to be precipitated. However, as common soils contain large amounts of Mg^{2+} and Ca^{2+} ions which both form insoluble salts with those $[M(OH)_4]^{x-}$ species, circumventing the problem (but, then, a kind of concrete can form, possibly clogging the pores and holes of the reactive barrier). Overall, there are so many electrons available for transfer in a controlled kinetic manner that some reactive barriers operate for almost 20 years now without too much maintenance or even need to replace the reactant Fe.

3) *Removing functional groups from organics by reduction*

There are many similarities between processes which occur in reactive walls and transformations in technical organic chemistry. Insofar as iron is also used for reducing nitro compounds to yield anilines (or azobenzenes, depending on conditions and solvents) while dialkyl sulfides or neutral amines—here produced in compost exposed to anaerobic conditions—will react with halogenated aromatic or aliphatic compounds to afford less halogenated hydrocarbons, sulfonium or ammonium salts.

After reactive walls had been conceived by Gillham in the late 1980s, the first large-scale device of this kind was constructed to clean soil contamination at the former Moffett Field Airbase (Calif., USA) in 1992. There are mainly organic contaminants, among which chloroorganics, then being usual solvents, like 1,2-dichloroethene, tri- and tetrachloroethenes, 1,1-dichloroethane and Freon 113 (1,1,2-trichlorotrifluoroethane) which is notoriously hard to oxidize, while non-halogenated aromatics like BTEX solvents are almost absent. The pollution came from leaking storage tanks of the said solvents, besides a method of collecting and recycling such solvents which there were applied for cleaning machines. Quite similar sites with chemical remains of machine (including tank-) and uniform cleaning also exist in Europe, for example, in Bernau next to Berlin, a remnant of the Red Army presence in the former German Democratic Republic (GDR), and this is also treated by a reactive wall.

Moffett Field, however, is the classical site of a large Fe-based reactive barrier and, moreover, there were rather intense investigations on the site and the (long-term) performance of this device. Let us hence discuss with this example how things are done: they started doing laboratory work on the relative performances of various brands of granulated raw iron concerning reduction kinetics, properties and substrate patterns. Finally, a mixture of various iron granulate diameters from Peerless Metal Powders Inc. (private company, USA) was selected. Tests gave half-lives⁶⁰⁾ for chlorinated hydrocarbon sol-

60) That half-lives can be defined for these reactions implies that the reactions display first-order or pseudo first-order kinetics, probably by the chlorohydrocarbon

molecule adsorbed to some relatively huge multi-iron site and become reduced there stepwise without intermediates becoming ever desorbed.

vents between some 20 and 50 min (C_2Cl_4) and 10 hours (dichloroethane). As a surprise, only the “large-scale” device, that is, the actual reactive wall installed at Moffett Field, also caused reduction of CFCs, including almost complete of Freon-113. The reaction wall is designed as follows:

At 7 m below the soil surface, above the level which limits the aquifer to the bottom, a concrete layer is introduced to produce the foundation of the construction, which is a very grave change in the structures of both soil and terrain. “Before” and “behind” the reactive wall, as defined with respect to the flow direction of ground water, a large permeable containment made of geotextiles encloses the reactive compartment against the soil volume. This geotextile “bag” is filled with the reactant which is *not* pure iron granulate (of 0.2–1.0 mm grain size) but a mixture with sand and fine gravel. This is done to avoid clogging and formation of a massive iron-rust aggregate; otherwise water can no longer pass through and be purified once iron oxidation begins. This geotextile/iron/gravel bag extends from the basis-forming concrete plate up to about 1.70 m below the surface, above this there is a coverage made from the very soil removed before. Yet one must make sure the ground water actually passes through the cleaning device. There are various measures which can be taken to assure this:

- The contaminated site may be encircled by the reactive wall completely (except of upstream) from surface down to the next layer underneath which is water-tight (clay, loam, bedrock, oil shale, etc.);
- Making use of natural pathways of groundwater flows, for example, along hill slopes;
- Injection wells, drainage ditches;
- The ground water flow may be actively propelled by electrokinetics.

At the Moffett Field site, injection wells are employed which simultaneously are used for taking samples to check the efficiency of purification. For reductions of simple chlorinated hydrocarbons the results mainly agree with those seen in laboratory-scale experiments, including the formation of vinyl chloride (which is carcinogenic) which only occurs at the start of the experiment, it came to a surprise that CFC 1,1,2-trichlorotrifluoroethane also reacts in the

- 61) 1,2-dihalogenoalkanes and alkenes react with metals faster than their 1,1-isomers. For the differences between a laboratory model and an actual reactive wall, recall that pH 11 is “adjusted” spontaneously only in large systems while it has to be controlled by man in the laboratory (cf. our experiments). While haloalkanes are very poor ligands (there are some isolable complexes of dichloromethane and 1,2-dichloroethane), the cleavage of a chloride during metal-induced reduction includes a primary chelate formation

which is possibly only with 1,2-dihalogenohydrocarbons and speeds up the redox reactions. Unlike more reactive metals like Al, Mg, Ti or Zn, sometimes also Cd (with acyl halides) and Bi, iron will not insert into C-Hal bonds, that is, dehalogenated hydrocarbons produced in a Fe-based reactive wall are not due to intermediate formation and thermolysis or protolysis of Fe alkyls. With halogenated alkenes, however, it is conceivable that π -complexes between Fe^{n+} and C=C double bonds are produced first.

large-scale device and 1,1-dichloroethane⁶¹⁾ also reacts faster. The success at Moffett Field caused many to also use reactive walls in treating various kinds and sites of soil contamination.

Among the model studies, the reduction of soluble chromates (like our own shown in Figure 3.5) merits consideration, as does the retention of radioactive wastes from civil or military nuclear technologies and fuel processing. Cementation and hydroxide/aquoxide precipitation change the state of so many elements in very complicated mixtures likewise as to remove the vast majority of them, even if nitric acid and organic ligands/extraction solvents are present, too, like with the remains of nuclear fission if subjected to fuel fractionation and reprocessing. Now hundreds of reactive walls using iron have been implemented all over the world. When compost walls or other preparations which afford sulfide are employed (Benner *et al.*, 1999), nitrate will be reduced to produce N_2 mainly, while high-pH reductions at both Fe and Zn will rather yield NH_3 and nitrogen oxides if the system is kept acidic.

When either the contamination goes rather deep or the aquifer is very thick, it would be a technical problem to dig a trench then to be filled with the mixture which constitutes the reactive barrier. Rather, Fe metal-containing granulate is suspended in the water used to pump the sludge and is thus pumped into sediment under high pressure. In addition, this automatically produces that mixture of Fe grains, sand and gravel necessary for the long-term activity of a reactive wall.

Fe is cheap, but weakly toxic and sufficiently strongly reducing to attack and passivate both heavy metal and organic pollutants by concomitant reductions. Products are summarized in Table 4.5.

Table 4.5 contains but such inorganic contaminants which have already been shown to be successfully tackled by Fe reactive barriers. A small addition of sulfate (10^{-5} M/l, corresponding to “saturated” $BaSO_4$ being present) considerably improves As retention on the laboratory scale (Nikolaidis, 2002) without involving microbiological effects like sulfate reduction, which forms As_2S_3 or As_4S_4 .

Most of the elements which are to be sequestered at neat Fe interfaces will turn into the metals thus (cementation), which are—except for mercury—insoluble in water while forming—once again except for Hg [this is why Hg is stored in iron (or plastics, glass) tanks]—alloys with Fe which additionally increase retention by the reactive barrier. Except for Hg and N which produces readily soluble NH_3 the elements are removed from ground water flows anyway. However, there is a problem with the precipitation of noble metals other than mercury in reactive walls: the cementation of Ag, Au or Pt (platinum group metals) causes some kind of shortcut in the reactive wall, reducing the overvoltage⁶²⁾ for hydrogen reduction so much as to “funnel” the Fe reductive capacities (i.e., electrons given away by Fe metal) mainly into H_2 production there-

62) The overvoltage is the thermodynamic activation barrier which must be overcome to produce dihydrogen H_2 on base metal interfaces. Due to this overvoltage, Fe, Zn or Cd are reasonably stable in water although their redox potentials are somewhat negative of H_3O^+/H_2O .

Table 4.5 Speciation and precipitation of metal and non-metal compounds at a Fe-based reactive barrier aiming to obtain speciation forms which would not dissolve in water and be (in best of cases) minimally toxic.

Pollutant	Stable speciation form in a reactive barrier	Product soluble in water?
Zn	Zn(OH) ₂	No
Cd	Cd ⁰	No
Hg	Hg ⁰	Minimally
Cr	Cr(OH) ₃	No
Mo	MoO ₂ or FeMoO ₄	No
Co	Co ⁰	No
Cu	Cu ⁰	No
Pb	Pb ⁰	No
Ni	Ni ⁰	No
Tc	Tc ⁰	No
U	UO ₂	No
NO ₃ ⁻	NH ₃	Yes
HPO ₄ ²⁻	FePO ₄	No
As	As ⁰ , FeAsO ₄	No
Se	Se ⁰ (FeSe ?)	No
Ag	Ag ⁰	No
Au	Au ⁰	No

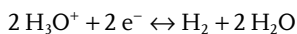
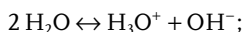
The quoted forms are those which will co-exist thermodynamically with Fe(OH)₂ at pH 11.

after.⁶³⁾ If we are to hydrogenate organic pollutants in groundwater, like halo- or nitroaromatics or PAHs, this even is an advantage, but it is definitely detrimental for cleaving soluble pollutions by less noble metals like chromium (as chromate in ground waters beneath leather tanning or galvanic factories). As you cannot look into soil, the processes which occur in a real reactive wall cannot be observed, even when involving colored species and color changes thereof; thus additional model studies like in Figure 3.5 were done on Fe-dependent chromate sanitation.

As noted above, the ground water around and inside the reactive barrier becomes alkaline owing to the reductive activity of the reactive wall itself: protons are taken from the protolytic equilibrium of water:

63) The same effect keeps a lead-acid accumulator from being rechargeable for an indefinite number of times: a cathode which consists of lead(II) sulfate—usually doped by antimony for keeping electrode dimensions constant [see the alloy introduced by Gutenberg (in 1445) for making printing letters—discharged state (as does the anode then) can no longer be reduced into Pb metal if there is no

overvoltage left for H₂ production]. Since Pb from natural sources (mines) invariably contains some silver, this Ag is going to migrate up to the electrode surface steadily upon repeated charging cycles, finally forming a thin film there. When this has happened, the accumulator can no longer be recharged, because putting a negative potential to the former cathode will liberate dihydrogen rather than lead metal there.



by being converted into H_2 with hydroxide ions remaining in solution [the same as happens in the violent dissolutions of alkali metals in water producing $\text{M}(\text{OH})$ solutions]. The latter OH^- ions get enriched, making the surrounding of the reactive barrier alkaline (like with every cathode). The resultant pH values of about 11 were taken for discussing element speciation in Table 4.5 also. Electron transfer and dihydrogen formation in a rusty wall become most efficient for reducing functional groups of and thus cleaving organohalogenes or nitrocompounds (both aliphatic and aromatic) when steel scrap is used rather than pure iron, the former usually containing several percent of Ni. Organohalogenes like tri- or tetrachloroethylene or chlorobenzene tend to be completely dechlorinated; in addition, the remaining organic compound is likely to be hydrogenated, too, making, for example, cyclohexane, cyclohexene and cyclohexanol⁶⁴⁾ from chlorobenzene, while nitrocompounds produce amines or oximes which are less toxic and rather ready to further microbiological conversions. Unlike formation of compost, that of peat and applications of either material in reactive barriers is an anaerobic process where sulfate-reducing bacteria (SRBs) produce H_2S . This will produce large redox potential gradients both vertically and horizontally along the reactive barrier while pH does increase like in Fe barriers, and for much the same reasons. Sulfides likely to experience retention include those of Zn, Cd or Cu, but not As (!), Fe, Mn or Al. While Fe and Mn can form sulfides insoluble in water or alkaline solutions also (but readily dissolve in acids), they are more likely to be retained directly by rotting biomass forming polymeric carboxylate matrices⁶⁵⁾ which make complexes hardly mobile or even become unable to be resorbed by roots, like the other two elements As and Al, getting included into ternary salts (thioarsenates and hydroxoaluminates, respectively) or directly sticking to the rotting biomass, given the stability of $\text{Al}(\text{III})$ polycarboxylate complexes.

Obviously the procedure, depending on the liquid phase exclusively, takes a substantial speed of ground water flow through the barrier (several score m/year). Apart from pumping in wells or using natural or constructed slopes, one can make the water moving itself by applying some voltage (direct current) to the soil. Then,

- 64) Similar pathways are taken with multiply functionalized aromatic such as 4-chlorophenol; here besides phenol its hydrogenation products cyclohexanone (cyclohexene-1-ol tautomer) and cyclohexanol are obtained all of which are more acceptable to heterotrophic bacteria than the original chlorophenol.
- 65) Cellulose from peat or freshly oxidized plants (compost) is turned into a kind of polyglucuronic acid, rather similar to

the structure of pectin (Habermehl, Hammann and Krebs, 2002) and which behaves as an cation exchanger; a procedure already described in the Holy Bible (Barka, 1978) which affords Fe and other complexes by metal extraction from sediment but no longer accessible to plant roots (Wandas, 2011). Humic acids originate and behave similarly (*ibid.*).

electrokinetic effects will make the water flow.⁶⁶⁾ Reactive walls can be designed as plugs or claddings to protect single wells and the water intruding them, also. Corresponding model studies were undertaken to control and relieve the As burdens in many wells in, for example, Bangladesh.

4.3.1.3 Conclusion

Reactive barriers are well-suited to treat a manifold of different soil contaminations (given there is equilibrium with groundwater and a minimum solubility of pollutant⁶⁷⁾). The advantages and disadvantages of the method are summarized in Table 4.6. Likewise, the principle, technique and setup can be applied to waters above the surface or those trickling to some spot. Then there will be not a “wall” in soil but the reactive filling forms some permeable dam in a drainage ditch which is percolated by the medium to be purified. Reductions give a chance to remediate organic compounds like freons or nitrocompounds which are most stable toward oxidants, causing cleavage of their typical—and problematic—functional groups. The reactive wall is capable of adjusting its pH to some value most suited to effect quite a number of reductions, like that of chromate, besides of hydroxide precipitations without additional measures. Several reactive barriers have been run for more than 15 years now, giving proof of long-term stability. Given ground water flows—or is made to flow—at some scores of m/year, underground contaminations which extend over larger areas (industrial grounds, landfills) can likewise be sanitized.

4.3.2

Pharmaceuticals in the Environment—Special Emphasis on Diclofenac (Voltaren™)—An Analgetic Agent with Difficult and Interesting Properties

4.3.2.1 The Problem

Among the about 100 000 different compounds used by humans for quite different purposes, some are intended to act in the environment (e.g., biocides) while others just get into contact with environmental compartments (e.g., as part of constructions, vehicles), fuels are exhaled after combustion and, finally, there are biological agents which are designed to cause their intended effects within some organism

66) This is the inverse effect of making some zeta potential by running water or other liquids through columns filled with some solid bearing charges on the surfaces of the solid particles. Here, typical voltages are of the order of 100 mV and neither it nor the reverse effect will work if there are no charges on the solid particles. This may happen at a certain pH (hence called the point of zero zeta potential; PZZP).

67) Very unpolar organic compounds, for example, PCBs or DDT, at $\log k_{ow} \approx 6$

display both very pronounced adsorption to the solid soil phase(s) and a water solubility of but a few $\mu\text{g/l}$, precluding sanitation by reactive walls altogether. However, both chlorobenzenes ($\log k_{ow} \approx 2.8$) and even less polar halonaphthalenes were removed successfully from polluted groundwaters, thus the practical limit is somewhere in between.

Table 4.6 Advantages and problems seen in applying reactive barriers.

Advantage	Problem
Many different pollutants respond to this approach	Substances “untypical” for soil are introduced; the local pH difference strongly alters soil chemistry and geobiochemistry (which microbes will persist next to the barrier at all?)
Simple technology, easy to construct, cheap (depending on material put into the wall)	Toxic, combustible or explosive gases may be vented from the barrier, including H ₂ , vinyl chloride, organofluorines, NH ₃ , with organic barriers also CH ₄ and H ₂ S
Little use of surface areas	Metals which were deposited as hydroxides rather than reduced cannot be taken to be localized forever as pH in and around reactive barrier will return to normal values (i.e., slightly to moderately acidic unless for marl or other carbonate soils) once Fe oxidation stops, thus hydroxides may undergo re-dissolution
Construction is stable and will operate for many years	
Adaptable <i>in situ</i> method	
It is likely that metals deposited by cementation will stick to the barrier for a very long time when it is left in the ground after the operating period	

but which leave the site of action eventually as such or as their metabolites by excretion: pharmaceuticals. In the aquatic environment, some of these pharmaceuticals are highly reactive or bioactive, damaging particularly organisms at levels about those actually seen in rivers now. Excretion would not necessarily mean pollution of the environment but sewage treatment plants can hardly cope with many of these compounds, letting them eventually pass into rivers and lakes.

Commonly employed pharmaceuticals which behave like this include steroids and various amines. Among the latter amines there are neuroactive agents including serotonin reabsorption inhibitors, stimulants and psychopharmaceuticals like anxiolytics, antidepressant agents and cures for cramps, seizures and epilepsy, like carbamazepin. All these, besides the blood lipid inhibitors, can be readily detected in open waters in both Europe, northern America, Japan and Australia, as they mostly escape sewage treatment (not even being substantially adsorbed to sewage sludge). Thus some property must be identified which offers a perspective for chemical attack during water cleaning treatment apart from microbiology. As mentioned before, many of these substances are (primary through tertiary) amines, or carboxamides and are often known to be susceptible toward 1e-oxidation path-

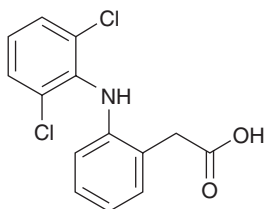


Figure 4.36 Diclofenac is an analgetic compound—an aromatic one like aspirin and ibuprofen—which is distinguished by both persistence and, apparently in contradiction, a

remarkable variety of functional groups bound to two aromatic rings and linked by reactive diphenyl amine moiety.

ways at moderate potentials in aquatic systems. The best way of inducing such electron transfer processes is photochemistry, perhaps augmented by a semiconductor interface. For reasons given below, the focus of our interest is with the aromatic amine (substituted diphenyl amine) diclofenac and compounds containing some of its structural motifs only.

Diclofenac is an agent that is used as a non-steroidal analgetic which cures muscle and joint aches by cyclooxygenase (COX2) inhibition and, besides, interferes somewhat with cyclopentenone (prostaglandine) signal systems. It is a short-hand—this way of naming compounds is quite typical for pharmaceutical agents—to denote 2',6'-dichloroanilinophenyl-2-acetate (Figure 4.36).

Although most diphenylamines undergo air oxidation readily, the anionic compound diclofenac (annual consumption of which in Germany is some 90 t) is quite stable, thus most makes it through a sewage treatment plant unchanged. As it hence does not undergo biochemical modification either and also is used in veterinary medicine (Oaks *et al.*, 2004), the compound will be found both in the carcasses of fallen animals and in aquatic sediments.

4.3.2.2 Toxicological Effects to Animals

There it poses a risk to birds consuming either carcasses or sediment, with certain vulture species living on the Indian subcontinent being most vulnerable. After taking up diclofenac with contaminated meat (i.e., eating dead animals which succumbed from some disease or ache even though they were treated with diclofenac and, possibly, other kinds of medication), these vultures would soon become unable to fly and would eventually die from renal failure causing uremia and visceral gout. Other causes of intoxication (Cd, Pb, organophosphates . . .) and accidents could be excluded from being lethal to vultures by autopsy in these cases (Oaks *et al.*, 2004).

Obviously the diaryl amine diclofenac here interferes with nitrogen-cycling metabolism and urea production or disposal in these birds (other birds, including birds of prey, tolerate diclofenac much better although at higher levels it is also toxic to dogs). Kidney damages due to diclofenac were also observed in fishes at levels $\leq 1 \mu\text{g/l}$ which is not too much above the average level detected in central

European lakes connected to urban centers unless there is intense UV irradiation promoting photochemical rearrangement.⁶⁸⁾ Xanthine oxidase, a Mo-dependent enzyme, is blocked by diclofenac (which also blocks another oxygenase enzyme, CO_x see above!) in certain varieties (typical of certain vertebrate species, some fishes and birds). Normally, xanthin (a N heterocycle) ring oxidation would end up as urea (with mammals including man), carbamoyl groups or eventually (in fishes, birds) NH₃; but uric acid piles up if this xanthin oxidation (and thus xanthin oxidase) is competitively or irreversibly inhibited, bringing about uremia, gout and damage or destruction to the liver, kidney, muscles and joints. In either way, food chains and nutrient cycles are compromised (more N loss to the environment, lower trophic chain lengths among consumers), with the decline of vultures in tropical climates also increasing the risk of epidemics spreading from rotten meat.

Even now, five years after the use of diclofenac in veterinary medicine was discontinued (banned) in India and Nepal in 2006, the decline of regional vulture populations continues, although it has slowed, suggesting either ongoing large-scale illicit use of diclofenac in cattle or the involvement of other reasons (agents) of intoxication in the vulture species most hit.

A substitute for diclofenac which is safe to birds of prey although not recommended for use in very young animals (or children) is meloxicam (Figure 4.37), a derivative of saccharine, from which it is actually prepared. Like diclofenac, meloxicam also acts as a cyclooxygenase inhibitor.

However, substitution is far from complete especially in medicine targeted at humans. Hence the degradation of diclofenac remains to be an issue in wastewater

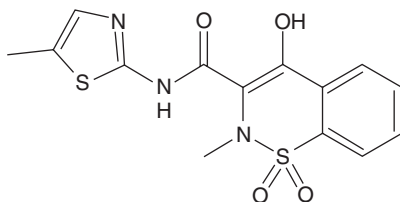


Figure 4.37 Meloxicam acts as a cyclooxygenase inhibitor.

- 68) Strictly speaking, the conversion of diphenylamines into carbazols and the equivalent 2-methyl biphenyls into fluorenes or 2-phenyl phenols into dibenzofuranes are not rearrangements but oxidative ring closures, leaving behind two H atoms. In open waters like Lake Greifensee near Zurich, the amounts of the corresponding carbazole are far larger than those of diclofenac itself. Thus, the behavior of carbazole was studied along with those of diclofenac and

diphenylamine in these degradation studies. Assuming the breakdown of one C_{aryl}-N bond in either oxidizing (h⁺ attack) or reducing (sonochemistry in formic acid), the plausible fragments (reaction intermediates) aniline, phenylacetic acid and 2,6-dichlorophenylacetate were also investigated. The last entry also gives some information on possibly effective treatments of auxine-type herbicides such as 2,4-D and 2,4,5-T (chlorinated phenoxyacetates).

treatment. As conventional wastewater treatment fails to degrade diclofenac, this poses some environmental problems; and it also should be considered a priority chemical. Given the corresponding lower limits for the amounts of chemicals which leak into open environments on German (>10 t/year in the territory of the then FRG back in 1982) or EU levels (according to REACH, >5 t/year in all of the EU since 2007), novel approaches on degradation up to mineralization were to be identified. Adsorption is not an option (otherwise it would occur in sewage sludge also) since diclofenac is fairly polar.

4.3.2.3 Novel Methods of Removing Diclofenac

In the following, two possible methods of removing diclofenac are presented.

1) Assisted photoelectrochemistry

Assisted photoelectrochemistry (Fränzle, 1992, 1996, 2003; Kokorakis, Fränzle and Hennig, 1998; Hennig *et al.*, 2001; Fränzle *et al.*, 2010) is meant to operate⁶⁹⁾ by semiconductor-supported ligand to metal charge transfer (LMCT) photochemistry using oxidizing (transition) metal complexes with spectral sensitization. Here, a metal complex is adsorbed to some broad-gap semiconductor ($E_{bg} \geq 2.4 \text{ eV}$) which itself transports charge carriers ("holes") to eventually oxidize some co-adsorbed organic compound while photochemistry takes place at the complex, which produces charge defects rather than in the semiconductor itself.

As a result, reactions can take place using long-wavelength (e.g., orange) or even near-infrared light while the limiting conditions concerning combinations of photoactivating complex ligands [L, e.g., halides (best, Cl and Br), NO_2^- , SCN^- , NCS^- , CN^- , OH^- , RCOO^- , glycinate $\text{H}_2\text{NCH}_2\text{COO}^-$ or some neutrals] at a given metal center and the semiconductor (e.g., Bi_2O_3 , Nb_2O_5 , CdS , ZnSe or Fe_2O_3); and reactions can be planned insofar as the relationship between ligand redox and photochemical properties is concerned, using Jørgensen's formula:

$$30 \cdot (\text{EN}_{\text{optLig.}} - \text{EN}_{\text{optMet.}}) + 10 \text{ Dq} + \text{aB} \quad (\text{energies in kK}^{70)})$$

and the relationship between $\epsilon_{\text{ox;rad.}}$ (for some data, see Isse *et al.*, 2011) and optical $\text{EN}_{(\pi)}$ for halido- ($\text{Hal} \neq \text{F}$), pseudohalido- and nitro ligands:

$$\text{EN}_{(\pi)} = 2.28 + 0.239 \epsilon_{\text{ox;rad.}} \quad (\text{L}^+ = \text{Cl, Br, I or CN}) \text{ or:}$$

$$\text{EN}_{(\pi)} = 2.25 + 0.246 \epsilon_{\text{ox;rad.}} \quad (\text{L}^+ = \text{Hal, } \underline{\text{NO}}_2, \underline{\text{SCN}} \text{ or CN}) \text{ (almost the same)}$$

69) There are photophysical experiments to corroborate this charge transfer mechanism (Kokorakis *et al.*, 2000; Hennig *et al.*, 2001); and ligand dissociation before recombination was also demonstrated.

70) 1 kK (kilokaiser) is a colloquial energy measure in spectroscopy though not

conforming to SI units. It corresponds to the quantum energy at $\lambda = 10 \mu\text{m}$ which is $E \approx 0.124 \text{ eV}$ per photon. Here we consider visible light of some 500 nm, that is $E = 20 \text{ kK} = 2.48 \text{ eV}$.

while:

$$30 \cdot (E_{\text{optLig.}} - E_{\text{optMet.}}) + 8 \approx \text{energy of reddest useful LMCT}^{71)} \\ \text{band (in kK once again).}$$

Hole injection occurs if the ligand radical is more oxidizing than the valence band lower edge of semiconductor sorbent in the given condition of solvent, proton activity, potential biases and so on, thus:

$$E_{N(\pi)} \geq 0.24 E_{\text{vb}} (\text{vs SCE}) + 2.27$$

When one knows the valence band edge potential of some semiconductor sorbent, one can thus select appropriate complexes for spectral sensitization. At Bi_2O_3 , with a valence band edge at about 1.4 V, ligands with $E_{\text{opt}(\pi)} \geq 2.6$ will cause hole injection into the sorbent (which also is an excellent sorbent, even applied as a stationary phase in chromatography, for organic compounds).

The kinds of organics which can be photooxidized in this manner include aldehydes (transferring part of the CO given away by R-CHO^+ formation and decay to the metal sensitizer center which produces reduced M carbonyls), various phenols, aromatic and aliphatic amines, PAHs, carboxamides and others. It also works with diclofenac, achieving complete mineralization.

2) Reductive cleavage using ultrasound

High-intensity ultrasound—intense enough to induce acoustic cavitation (Lickiss, 2000)—periodically produces small bubbles in solutions or sludges which then are rapidly (thus, adiabatically) compressed to reach p and T values under which free radicals from the solvent attack and destroy (mineralize) organic pollutants if the latter get into the bubbles (typically: 5000 K, p = some 1000 bar, even in focal places of a humble ultrasound cleaning bath) which they would not do if forming either cat- or anions. Accordingly, only neutral species can be processed inside such bubbles. However, this does not imply that oxidations, for example, by OH radicals formed from water, are the only transformations feasible by sonochemical means. In fact, hydrogen co-produced from sonolyzed water can be employed in reductions. As diclofenac is a weak acid, an acidic pH is required to maintain the neutral state accessible for sonolysis.

Now, there are quite a number of organic pollutants which are rather resistant toward oxidation, like nitro or halogenated organics, but which could

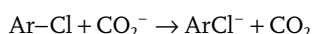
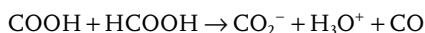
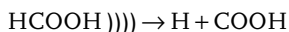
- 71) While there are fairly intense ligand to metal charge transfer (LMCT) transitions even beyond 1000 nm wavelength with some complexes, like platinum group metals (rhodium and osmium, respectively) complexes $[\text{RhCl}_6]^{2-}$ and $[\text{OsI}_6]^{2-}$, $[\text{OsI}_5\text{Cl}]^{2-}$, it must be pointed out that all these complexes are already

thermochemically unstable, decomposing on storage in either crystals or solution under metal ion reduction (which thus need no longer be induced by electromagnetic irradiation!), for example, according to $2 \text{OsI}_6^{2-} \rightarrow \text{Os}_2\text{I}_3^{3-} + \text{I}_3^-$ (triiodide) even much below 0 °C.

possibly be treated by reduction. This can be achieved by cathodic reduction, sometimes by enzymes, often at a reactive barrier ("rusty wall"); and it should also be feasible when sonolyzing a solvent fragmentation of which easily affords H atoms and, in the best of cases, additional strongly reducing components capable of cleaving and/or reducing such tricky substituents. In addition, organic solvents with corresponding properties might more readily dissolve organic pollutants. Very strongly reducing by-products of solvent sonolysis would include hydroxyalkyl radicals ($R-CH-OH$, from primary alcohols), ketyls [$R-C(OH)-R'$, from secondary alcohols], CO_2^- anions (from formic acid, oxalate semiesters), or $^*CO-NH_2$ (from carboxamides), all of which, like H atoms, have formal reduction potentials around $-2V$ versus SCE.⁷²⁾

This would suffice both to reduce nitro groups and to de-halogenate chloro- or bromo-organics. For simplicity and convenience, and because just two highly reducing components are produced, formic acid was selected as reaction medium to be subjected to sonochemical processing even though it—much like water—is so polar as not to dissolve many kinds of organics either.⁷³⁾ Actually, diclofenac only reluctantly dissolved to produce a grayish solution, which, however, became clear soon during sonication. Diclofenac was determined to undergo degradation in these conditions, as did other halogenated hydrocarbons. Aniline or 2,6-dichloroaniline were not detected among possible intermediates.

Both H atoms and CO_2^- anions are formed by sonolysis and are capable of cleaving $Ar-Cl$ bonds and diphenyl amines, as evidenced by experiments where these species were produced in other manners while chloroarenes are fairly readily reduced (Isse *et al.*, 2011):



72) Since $HCOOH$, like water or methanol, is a well-ionizing solvent which dissolves many simple salts producing highly conductive solutions (Fialkov, 1979), attempts to directly observe the presence of strong reductants by adding reducible rare earth elements³⁺ ion salts which, then, would change or acquire color [e.g., colorless $Yb(III)$ added as the triflate $Yb(CF_3-SO_3)_3$, to turn into dark-red Yb^{2+}] by CO_2^- reduction upon turning on ultrasound, failed as the precursors once again cannot propagate into cavitation bubbles.

73) For example, $HCOOH$ does not mix with alkanes—neither do formamides including DMF, hence H bridges do not matter but

this is a polarity effect—and cold formic acid would also remain separated from benzene or toluene. The latter allows for the extraction of metal carbonyl (halide) complexes prepared in formic acid into toluene by cooling and adding appropriate long-chain ammonium ions like $(n-C_{10}H_{21})_4N^+$ (e.g., the perchlorate or bromide). Extraction here means purification of the complexes also; quaternary aryl phosphonium or arsonium salts must not be used as they react with $HCOOH$, being reductively degraded (cleaving aryl-pnictogen bonds) all the way to the highly toxic gases PH_3 , and AsH_3 , respectively (Fränzle, 1992).

$\text{ArCl}^- + \text{HCOOH} \rightarrow \text{ArH} + \text{Cl}^- + \text{COOH}$ while:

$\text{Ar}_2\text{NH} + \text{CO}_2^- + \text{HCOOH} \neq \text{ArNH}_2 + \text{ArH} + \text{COOH}$ (see above).

Aqueous sonochemical degradation of chloroform CHCl_3 was done in different alkaline solutions; the results taking NaOH which, being volatile, can propagate into cavitation bubbles, and Ba(OH)_2 which cannot do so. The latter additive was used to show that neither carbonate nor oxalate was formed during CHCl_3 alkaline sonolysis, while substantial amounts of HCl were, steadily decreasing as the pH of the solution rose.

4.4

Energy—One of the Biggest Challenges of the Twenty-first Century. The Need for Renewable Energy

4.4.1

The Problems

From the industrial revolution onwards certain kinds of energy sources have been widely used while new ones and novel methods of energy conversion have been developed [electric motors, generators and alternating current (AC) grids in the nineteenth century, fuel cell, nuclear fission energy and semiconductor devices for converting various kinds of energy into electricity in the twentieth]. Now fossil fuels run scarce—as does uranium-235—and meet increasing criticism due to the climatic (greenhouse) effects of both methane and the principal combustion product, CO_2 . Hence regenerative resources like wind and solar energies, running and falling water (hydropower), biomass processed in some way and geothermic energy are in a position to replace crude oil, natural gas, coal and uranium step by step, depending on both technological innovations⁷⁴⁾ and political decisions. Thus we will contrast the problems associated with conventional sources of energy to the challenges and chances linked to renewable ones.

4.4.1.1 Energy Depletion of Fossil Fuels

Given the relativeness of time and the notorious “difficulty to make predictions which refer to the future”, what does it say that classical fossil resources will run out in the foreseeable future? Putting this into proper context means to distinguish between “reserve” and “resource”: “reserve” just encompasses those deposits of

74) Here, technological innovations are not meant to require still fundamental inventions to render some renewable resource useful for energy (electric current) “harvesting”. Rather, this is about making existing technologies cheaper and to overcome specific material problems, like device corrosion and fast “blocking” of underground heat exchange pathways with

geothermic energy and storage in a easy to handle form (methanol?) for both solar energy and biomass or using less toxic and less brittle semiconductors in much thinner layers in photovoltaics [thin-film cells based on either copper indium dichalcogenides (chalcopyrites) or organic semiconductors].

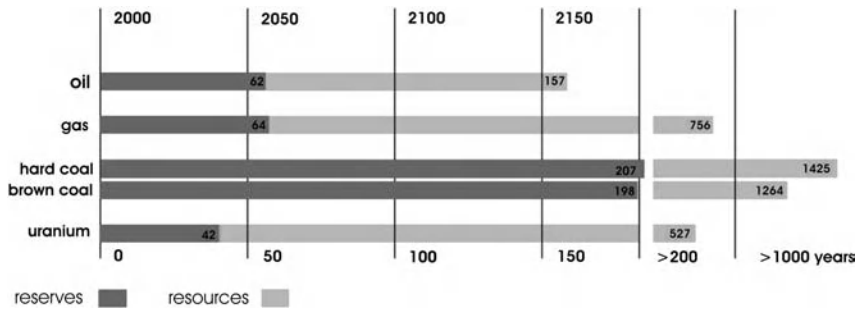


Figure 4.38 Predicted reserves/resources of fossil energy carriers from year 2000 onwards (Federal Institute for Geosciences and Raw Material Research, 2009).

energy carriers which are actually known and can be really accessed following both technical and economic criteria.⁷⁵⁾ “Resources”, in contrast, are those energy carriers either already discovered⁷⁶⁾ or *reasonably believed* to exist from geological arguments in the Earth’s crust,⁷⁷⁾ but which cannot be exploited right now for either technological or economic reasons. Given this distinction, the residual economic lifetimes for traditional forms of the energy carriers oil, natural gas, brown and hard coal or uranium given in Figure 4.38 are obtained.

Counting from year 2000 onwards, the German Federal Institute for Geosciences and Natural Resources estimated in 2002 that reserves of oil, natural gas and uranium will last for just another 40–65 years. Reserves of both hard and brown coal will still last up to 200 years, whereas the *resources* of coal and gas and uranium will last more than 200 years. Things are more critical with crude oil reserves, which will be gone within 60 years while resources are estimated to go for 160 years at best. The data and predictions in Figure 4.38 do not cover and include the energy consumption of current growth regions (BRICS states like Brazil, Russia, India, PR China, other Latin American countries), leaving us with the conclusion that we are left with much less time to change our bases

75) In the pre-1973 world of US\$2.70 per barrel of crude oil (some US\$19 per tonne) it would have been considered a fancy to try to extract oil from shales or sand, drill below the deep seafloor (now done always in the Atlantic Ocean: Mexican Gulf, off Brazil, Angola) or in remote arctic regions. Still now, the meaning of underground hard coal production or making access to very deep natural gas deposits is doubtful. While oil production from oil sands (Alberta Province, Canada) now is economically viable—yet still an ecological disaster in a sensitive surrounding—other methods of accessing certain fossil resources probably

never will: it simply takes more energy to extract and process traces of ^{235}U dissolved in seawater than can be obtained from its fission afterwards.

76) These become increasingly scattered: not a single “elephant field” of crude oil was spotted after the 1960s anywhere in the World!

77) Due to the difficulties and risks associated with drilling either below some 9 km underground or into active magma regions, most of the tremendous amount of geothermic energy can never actually be used. Hence, also for fossil resources we are left with what is in the crust and ocean (floor).

of energy supply altogether. The resources of crude oil are much disputed. Apparently, most of the additional stockpiles—beyond established reserves considered a few years ago—simply do not exist. Speculation on oil term markets is considerably influenced by this insecurity of affairs while the big oil companies obviously produce an exaggerated picture of resources rather than make speculation go its way.

Another matter is the regional distribution of these reserves/resources all around the globe (Figure 4.39; Federal Institute for Geosciences and Raw Material Research, 2009): the problem is obvious, and everybody is aware of it, with crude oil but there are biases/imbbalances also with hard coal. Considering the total energy stored in coal, some 60% of it rests⁷⁸⁾ with brown or hard coal and the smaller part is included in liquid and gaseous hydrocarbons. The crude oil which may reasonably be produced by current technologies amounts to 6682 EJ,⁷⁹⁾ a little less than that for natural gas (7136 EJ). The total energy from conventional fossil energy carriers (resources combined) would be some 448 289 EJ, 97% of these resources being hard or brown coal. Besides the above-mentioned conventional energy carriers, there are substantial amounts of other ones such as oil sands, oil shales, tars and other kinds of most heavy, most condensed oils, natural gas from dense storage sites, carbon deposits (adsorbed) or aquifer waters, plus gas (CH₄) hydrates on deep shelves (below some 350 m of seawater or in the uppermost sediments down there) reserves and resources of which correspond to an energy equivalent of 2368 EJ and 116 270 EJ, respectively (Federal Ministry of Economics and Technology, 2010).

Most of industrial activities now depend on oil, as do almost all traffic systems, be it airplanes, ships or cars. Oil getting scarce thus not only causes prices to rise but there will also be ramifications for the workforce in petrochemical branches and political implications. The largest share of oil (2005), some 742 billion barrels, is located in central and southern Asia (Bangladesh, Bhutan, India, Maldives Islands, Nepal, Pakistan, Afghanistan, Sri Lanka, parts of Iran). Considering the global oil reserves according to BP (in 2005), this translates into 62% of global

78) Note that the efficiencies of power plants differ considerably among these energy-carriers, hard coal and gas-steam plants being superior to the others ($\eta_{el} \geq 55\%$).

79) 1000 EJ (exajoule) = 10^{21} J. Standard heats of formation of the compounds/mixture/combustion products involved:

CH ₄	-50 kJ/mol
C (graphite)	zero [by definition (standard state of an element)]
"CH ₂ " (fraction of crude oil)	≈ -20 kJ/mol
CO ₂	-394 kJ/mol
H ₂ O	-237 kJ/mol

Thus one mol (44 g) of CO₂ produced from combustion of natural gas (CH₄, essentially) yields 818 kJ, from crude oil some 611 kJ, from coal just 394 kJ. The annual global anthropogenic CO₂ output is of order of gigatons (10^{15} g, Pg), with the atmosphere containing some 770 Pg of it now, considerably more than which is tied up in living biota (about 610 Pg). One gigaton of CO₂ from hard coal, crude oil and natural gas natural translates into somewhat less than 9.0, 13.9 and 18.6 EJ of thermal energy, respectively. So actually combusting the above estimated resources would leave us with some 50 000 Pg, that is, 65 times (!) the present CO₂ inventory of the atmosphere.

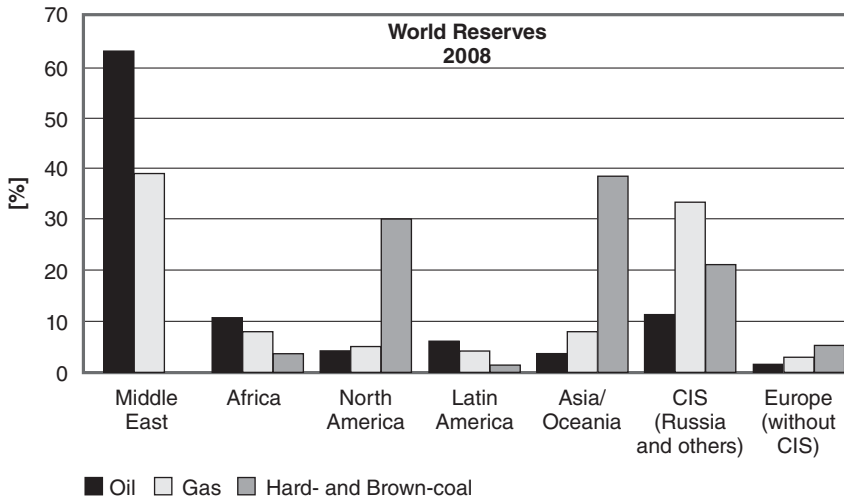


Figure 4.39 Estimate of the regional/continental distribution of oil/gas/coal reserves (Federal Institute for Geosciences and Raw Material Research, 2009). As for CIS states (former USSR except of Baltic states

and Georgia), the biggest share is with just three of them, Russia (the biggest oil producer in the world now), Azerbaijan (both oil and gas), and Turkmenistan (almost gas only).

stockpiles whereas north America commands just 5%, being one of the metaregions scarcest in oil besides Asia/Pacific and Europe.

With oil getting scarce, a one-sided economic dependence on the Middle East poses increasing political risks, causing everybody to consider oil and gas resources located elsewhere and how they and additional geological goods might be obtained. Thus, the recently growing geopolitical interests in the Arctic region, which will become void of drifting ice during the next 20 or 30 years due to climate change. According to the United States Geological Survey (US Geological Survey, 2008) some 30% of natural gas and 13% of crude oil are located there. However, most of these are located far offshore [the remainder already exploited for decades in Russia (Taimyr Peninsula) and Alaska], with most of the gas being in Russian Federation while oil is scattered among Canada, Alaska and Greenland (still partly governed by Denmark). Though very large, these deposits are not considered to relocate most of production activities from the Middle East, experts say (USGS, 2008). In addition long transport distances (thus, costs) and adverse weather and climate conditions pose grave problems. Everybody still is aware of what can happen with deep sea-based oil production, considering the Deepwater Horizon catastrophe of April, 2010, environmental concerns translating into larger political obstacles, higher insurance fees and eventually less consumer acceptance.

That the so-called peak oil level where global oil production reached its maximum ever was reached already in the beginning of this twenty-first century is evident from a depiction of development of oil production from 1930 until (predicted) 2050 (Figure 4.40): scarce oil means there will be no more cheap oil. Until the beginning

Delivery and detection of oil

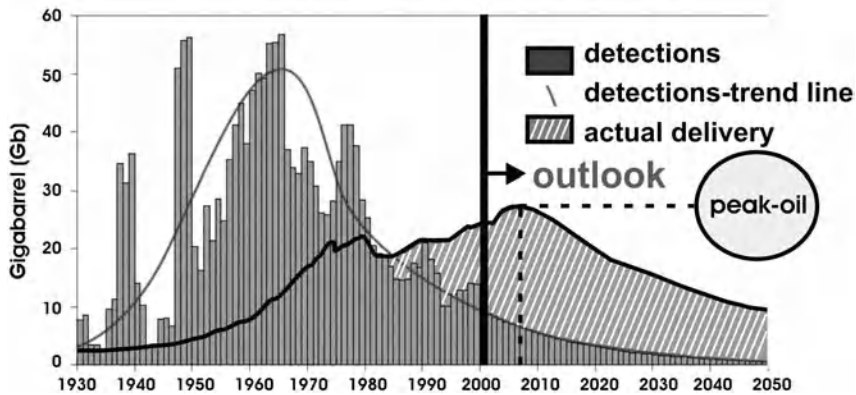


Figure 4.40 Oil findings and delivery rates 1930–2050 with the outlook after Campbell (2006). Calculated is the delivery rate per year by the Association for Peak-Oil and Gas Studies,

Germany; Data from Langwell (2002). Peak-oil: point of time when the maximum rate of global petroleum extraction is reached. (Modified figure by Blum, 2005).

of this twenty-first century, one barrel of oil commanded between US\$20 and a maximum of US\$40. The financial crisis made it (Brent) rise up to US\$147 after 2007. Declining somewhat, it is now (2011) stabilized around US\$100. In the long term it is more likely to increase again, having severe drawbacks on economic conditions in industrialized countries especially.

Figure 4.38 tells us that hard and brown coal reserves are to last another about 200 years, rendering coal-fired power plants most attractive if it were not for coal being one of the most polluting sources of energy. Combustion of coal produces plenty of CO_2 , and therefore it contributes to the anthropogenic part of greenhouse effect warming of our atmosphere.

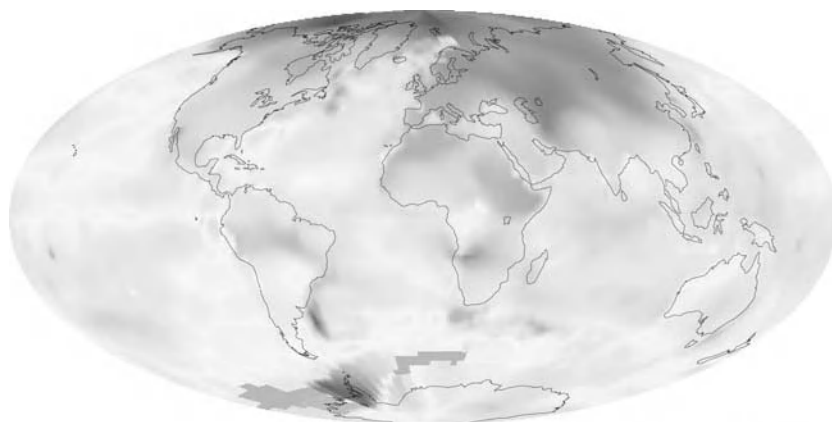
4.4.1.2 Climate Protection

CO_2 is one of the most prominent greenhouse gases in the atmosphere, contributing to heating⁸⁰⁾ the atmosphere and thus the Earth's surface. Present work is concerned with separating, sequestering and depositing (apart from atmosphere) combustion-formed CO_2 , see Section 4.1.2 on "CO₂ reduction" dealing with these carbon dioxide capture and storage (CCS) methods, which mostly are still in an early stage of development.

A global increase of average atmospheric temperatures has now been seen for decades, Figure 4.41 displaying the distribution of this effect for 2000–2009 as

80) There is both a natural and an anthropogenic (share of) greenhouse effect. CO_2 , produced by animal respiration, wildfires and volcanoes, is a natural (<300 ppm) component of the

atmosphere, heating our planet from a radiation equilibrium ("blackbody") value of some -18°C to a global average of $+15^\circ\text{C}$, that is, by a considerable 33°C .



Source: NASA Earth Observatory

Figure 4.41 Regional distribution of relative greenhouse effect warming. The map shows the 10-year average (2000–2009) global mean temperature anomaly relative to the 1951–1980 mean. The largest temperature increases

are in the Arctic and the Antarctic Peninsula. The darker the gray shades in the picture from NASA (Voiland, 2010), the larger the increase in local average temperatures.

compared to the reference timeframe of 1951–1980. Satellite measurements by the NASA Earth Observatory show the largest increases of the average temperature within the Arctic parts of the Northern hemisphere, besides some parts of Antarctica. Between the beginning and end of the twentieth century the average increase was $0.74 \pm 0.18^\circ\text{C}$.

Time is imminent for rethinking energy production with a focus on sustainability in all ecological, economic terms and social acceptance. Man-made radiative greenhouse forcing has been established for more than 20 years now. It causes enhanced glacier meltdown rates in all the Arctic (Greenland actually turns green again), Alpine and other mountainous regions, with the sea level rising (both due to meltdown waters and to thermal expansion of warmed surface water) and with more frequent droughts causing limnetic waters to evaporate often completely. We also should be urged and obliged to seriously think about what we are doing if, as some scientists still maintain, this is a normal climate excursion as occurred in the later Middle Ages. It does not take too much proficiency in natural sciences to acknowledge the problems associated with industry emitting greenhouse gases while striving to maintain and enhance our common well-being. Destruction of the environment, along with exploitation of developing “Third World” countries were an issue already 40 years ago, prompting the first Conference on the Human Environment at Stockholm (Sweden) on 16th June 1972, initiated and organized by the United Nations. Twenty years later, in 1992, the most comprehensive global conference on such issues ever held, the *United Nations Conference on Environment and Development* (UNCED) took place in Rio de Janeiro. 178 countries dedicated themselves to the Agenda 21 program to oblige the 118 more developed countries to environmental restoration, preservation and social development. Their aims are

to meet the challenge of global warming, pollution, biodiversity and the inter-related social problems of poverty, health and population. The Agenda 21 program furthermore encompasses the construction of a network of “new and equitable global partnership through the creation of new levels of cooperation among States, key sectors of societies and people, while working toward international agreements which respect the interests of all and protect the integrity of the global environmental and developmental system.”

In 1997 the World Climate Summit was held at Kyoto, Japan, focussing on the future climate protection policy and measures. The 158 states which had so far signed and ratified the Framework Convention on Climate Protection and six “observer states” had sent a total of almost 2300 delegates, plus another 3900 observers from non-governmental and other international organizations (NGOs) and 3700 journalists from global media, making a total of close to 10000 (United Nations, 2011). The Kyoto process unleashed by this huge meeting now describes the attempts to maintain climate protection agreements beyond the Kyoto protocol, which runs out in 2012, and to do so in a way which still is safeguarded by agreements of international law.

The industrialized states listed in Appendix 1 of the Kyoto Protocol agreed to reduce their collective greenhouse gas emissions by 5.2% from the 1990 levels by the year 2012. The common (purported) aim of the international community is to limit the increase of global average temperature within 2 °C.⁸¹⁾ The progress made so far is modest at best, real successes still to be awaited. The subsequent United Nations Climate Conference at Copenhagen (Denmark) in late 2009 saw just a communiqué of minimal consent without any mandatory aims in CO₂ reduction although the “two degree aim” was once again acknowledged to be worthwhile.

4.4.1.3 The Role of Nuclear Power

The Fukushima (Japan) sequence of catastrophic events began on 11th March 2011 [struck by the strongest earthquake ever recorded in Japan (Richter magnitude 9.1), causing coolant pipes to break and thus starting a sequence of reactor core meltdowns in at least three adjacent nuclear power plants (NPPs), then (10 minutes later) hit by a tsunami destroying control of events altogether and finally the uncooled reactor systems exploding one after another, releasing large amounts of radioactivity and visibly destroying reactor block 3] people reconsidered the risks of nuclear energy all over the world, although with grossly differing political consequences.

Now introduced into the International Atomic Energy Agency (IAEA) accident level VII, the events at Fukushima were set equal with the Chernobyl disaster [April 1986, Ukraine (officially: the Ukrainian Soviet Socialist Republic)] and considered worse than the explosion of a nuclear fission waste storage tank at Kyshtym in 1957 [near Chelyabinsk, Urals, in the then Russian Soviet Federative Socialist Republic (RSFSR), (parts of USSR); level VI accident] which delivered such large

81) By now it has become most doubtful whether this “two degree aim” can be kept at all. In addition, it has been proven that even an aggressive forestation policy could not cope by photosynthetic absorption (assimilation) with the present upsurge of CO₂ produced.

amounts of ^{90}Sr [several exabecquerel (EBq: 10^{18} Bq)] that an area of some 15 000 km² had to be abandoned for any human use up to now. Japan is known to be tectonically most active, prompting the authorities and engineers to consider earthquakes up to Richter magnitude 7.9 in their designs.⁸²⁾ The Fukushima earthquake was far stronger than this. The tragedy was increased by a tsunami caused by this quake; it took thousands of lives in cities and villages near the coast but most likely the crucial damage was already done to Fukushima NPPs by the earthquake, though the NPP area was inundated soon after. Certain radionuclides, mainly highly volatile ones,⁸³⁾ were released; that core meltdowns had occurred was first contested and then confirmed by Japanese authorities only 2.5 months later. Including those still missing, their whereabouts unaccounted for but unlikely still to be alive, there were some 23 000 fatalities due to quake and tsunami, and several workers received massive radiation damages during cleanup and a nuclear catastrophe is still looming ahead. The number of people forced to abandon their homes and jobs at Fukushima and Iitate provinces [40 km northwest Fukushima

82) Two matters demand further consideration here:

- 1) What causes, for example, the main coolant pipes to break is acceleration and the mere amplitude of dislocation combined with inertia, that is, parameters rather covered by the “old-fashioned” Mercalli scale of earthquake intensity, with Mercalli 13 denoting accelerations larger than that of Earth’s gravity. Such quakes have actually happened; for example, the Easter quake of 1964 in Central Alaska (there is a very impressive movie showing cars and humans and even some homes losing contact with the ground during the quake). In contrast, Richter scaling gives the energy unleashed by a quake [or a landslide or an underground explosion (be it chemical or nuclear in origin)] in a logarithmic way: Depending on the depth of the epicenter, that is, the amount of matter located above the vibrating or breaking sample of crustal matter, accelerations due to a given amount of tectonic energy can be quite different: the “fairly moderate” Haiti quake of February, 2010 (Richter 7.1), became a real killer not because of its energy but because its epicenter was located just a few kilometers below the surface, producing a massive acceleration, thus aggravating the effects of non-adapted architecture. Inertia also is a matter of dislocation

of the ground which provides a kind of reference frame, physically speaking, to which any device which can vibrate and so forth will respond: this dislocation was about 2.5 m in Japan on 11th March 2011, that is, much larger than in the even stronger (more energetic) earthquakes at Chile in 1960 (Richter 9.5) and Sumatra at Christmas 2004 (Richter 9.3).

- 2) At least two NPPs, one of them in Japan, had already experienced earthquakes exceeding these limits of design: at Niigata (northwest Japan) and at then Leninakan in the Armenian Soviet Socialist Republic (SSR) in 1988. So the design was obviously short of reasonable expectations [in central Europe, the German, Swiss and French NPPs next to the Upper Rhine rift valley do not take account of the fact that there Basle City was almost completely destroyed by a quake in historic times (in 1356)].

- 83) ¹³¹I, ^{134,137}Cs and some noble gases, traces of ¹³²Te but not Sr, Ba, rare earth elements. Apparently the temperatures during core meltdown did yet not suffice to vaporize alkaline earths or rare earth element compounds (cesium gets highly volatile as a hydroxide, CsOH molecules sublimating as easily as NaOH, KOH do), nor did volatile chlorides form after NaCl solidified (the NaCl came from seawater pumped inside to cool the reactor cores).

(that means NPP site not Fukushima town!)), probably forever, is more than 80 000 now, that is, close to the number of people made homeless due to the Chernobyl accident. Responses in different countries were different: while (either politicians or citizens) in certain countries started to abandon energetic uses of nuclear fission (Germany, Switzerland) or reaffirmed prior decisions of this kind [New Zealand, referendum in Italy with a 94% (2011) turnout, Belgium], others chose to keep a pro-nuclear course or even kept up decisions to build national first-ever NPPs (Poland).

The classical argument in favor of nuclear energy production is that it releases much less CO₂ as compared to oil, coal or natural gas power plants, enabling economies to meet Kyoto ends more easily. For certain countries which produce nuclear fuels but command few other natural resources,⁸⁴⁾ there is the bonus of apparent independence; this includes Japan. Nuclear energy is rather “compact”, a GW class power plant taking a few hectares at most, which is important in countries as densely populated as Japan (or India, or Belgium), with Japan covering a total area hardly larger than that of Germany (372 000 km²). Next to the United States (104) and France (59), Japan has the largest number of NPPs (53, from which the six at Fukushima and three to be shut down at another most earthquake-prone site must be subtracted, so effectively it is 44) due to a experience from the 1970s: the OPEC oil crisis in 1973, rapidly increasing the prices of crude, of course hit all the already then industrialized countries except for those producing sufficient fossil fuels of their own (Canada, Australia) or relying on other sources mainly for different reasons (Norway, New Zealand, South Africa) but worst so in Japan: in fact, there were large-scale electricity shutdowns badly hurting Japan’s economy. Hence Japan—once again in its history—became eager for independent supply, planning to build yet more NPPs before Fukushima happened. By now, unlike France, Belgium, the United States or formerly Lithuania,⁸⁵⁾ where it is 60% or more, Japan takes about 30% of its electricity from NPPs. Figure 4.42 gives the global pattern of distribution of NPPs which is almost complete [note that there are: (i) considerable differences in electric outputs of individual plants and (ii) some plants primarily meant to produce radionuclides rather than electric-

84) In the European Union the Czech Republic presently is the only state to mine domestic uranium ores, globally large producers being differently organized and reliable in political terms [Australia, Canada, USA, Kazakhstan, Niger, Gabon (central Africa)].

85) In times of Soviet dominance, Lithuania even had the largest NPP in the world, a 2400 MW_e-plant at Ignalina (now Visaginas), whose construction was of the notorious (Chernobyl) RbmK (*reaktor bolshoy moshchnosti kanalniy*: high power channel-type reactor) type. Relying on nuclear energy by >70% shortly after regaining independence, Lithuania had to

close down this plant as a precondition for joining European Union, as Bulgaria had with Kozloduj. Now, Lithuanians plan to erect a new, similarly huge NPP at the same site next to the border triangle with Latvia and Belarus to supply all of the three Baltic states, even though Latvia now is the European Union’s champion in regenerative energy supply, producing almost 40% of its (admittedly rather limited) demand mainly from hydropower, wind and some biomass use, and hard suffering from the financial crisis (much like Ireland and Greece but less perceived to do so since they still maintain their own currency, the Lat).

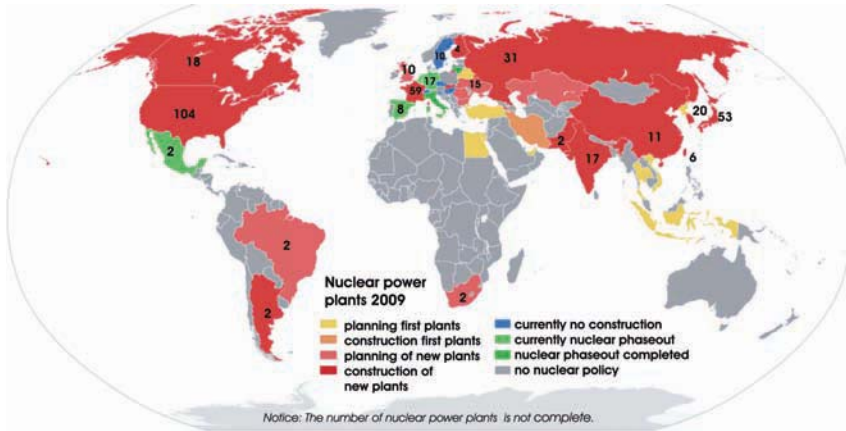


Figure 4.42 Nuclear power worldwide in 2009. The figure was transferred from Wikipedia; the number of nuclear power plants was added by collecting information separately from Wikipedia. The number of nuclear power plants is not complete.



Figure 4.43 The ten states (dark gray) which produced the largest amounts of uranium ores in 2008. Besides the spatially largest states outside of South America (and except for China, India), most are located in Western Africa, including Gabon (Central Africa) whose ultrahigh-grade (> 60% U) deposits at Oklo and neighboring sites gave rise to natural reactors some two bio. years ago (map from Wikipedia.de).

ity although they are connected to the public current grids (e.g., Dimona in southern Israel)]. The total number is about 450 NPPs.

As shown above (Figure 4.38), uranium reserves are to last for just about another 30 years from now (2011), adding another problem to safety concerns and disposal of radioactive wastes (see below) associated with nuclear (fission) energy. The increase in prices during the past five years even relatively surpassed that of oil, the process probably going on as demands for uranium did not yet reduce considerably on a global scale after Fukushima. Figure 4.43 gives a map showing the ten most prolific uranium-mining countries (by 2008).

Let us turn to the third issue associated with nuclear energy: radioactive wastes. These are produced by all nuclear fission and are then located in: (i) “used” (irradiated) fuel rods,⁸⁶⁾ (ii) neutron impact on non-fissionable ^{238}U , (iii) on construction materials (from Zircalloy to concrete) and (iv) the first decay products, sometimes dissolved in activated wastewaters and in dissolution residues (nitric acid) from nuclear fuel reprocessing (now banned in both the United States and Germany). All of these must be disposed of and stored until their loss of radioactivity toward stable products is essentially complete. The case is not at all settled, there are no operating final deposit sites but just such ones meant to contain (withhold) the waste for a few decades. Elsewhere, obviously radioactive waste solutions were discarded into the open sea or rivers both after accidents and routinely during nuclear reprocessing [Windscale/Sellafield (UK), LaHague (France), Mayak near Chelyabinsk (Russian Federation)], not to mention simply dumping discarded entire reactors from nuclear-powered submarines into the sea, with or without the rest of the vessels . . . What can be done responsibly with nuclear waste instead?

The periods of time over which radionuclides from fission reactors must be stored and safeguarded are outright unimaginable and far beyond any other time-frame of political or economic planning: there are nuclides with half-lives of several million years (^{94}Nb , ^{129}I , ^{237}Np) so they will present a danger for 10^7 years or the like.⁸⁷⁾

Here are some examples:

• Uranium	^{238}U	4.468 bio. years
• Uranium	^{235}U	704 mio. years
• Iodine	^{129}I	15 mio. years
• Neptunium	^{237}Np	2.144 mio. years
• Plutonium	^{239}Pu	24 110 years

While actinoides [from the third, protactinium (Pa, $Z = 91$) onwards] generally are extremely chemotoxic, this only matters for long-lived nuclides like the natural uranium isotopes, ^{237}Np , $^{242;244}\text{Pu}$ or $^{247;248}\text{Cm}$. In the other cases, say at $T_{1/2} \leq 10^5$

86) A fuel rod in a nuclear power plant is a metal tube (Zr mainly) filled with cylindrical sintered pellets of UO_2 or some mixture of UO_2 and PuO_2 ; metal alloys or other compounds (carbide UC_2 , hydride UH_3) are used in minireactors only. After a while a fuel rod is “spent”, reducing the ^{235}U content from the original 3.5% to some 1.3% while 1.0–1.5% of plutonium—most of it fissionable also—were produced from ^{238}U *in situ*. Although use could be continued by further pulling out the control rods which absorb excess neutrons, it would be no longer safe to work with such rods. Thus they are replaced, usually a third of them every year or so. The “spent” rods are

stored for several decades, usually next to “their” reactor to get rid of the highly active short-lived isotopes of high yields, for example, $^{141;144}\text{Ce}$ and $^{103;106}\text{Ru}$ and ^{91}Y , then either processed or put into a final depository (if there is one, by now only in Finland).

87) With ^{237}Np , of which there are many tonnes now, and ^{243}Am (americium, of which tens of kilograms exist) there is an additional problem: during very long storage, enriched samples of either nuclide will spontaneously turn into fissionable materials (^{233}U and ^{239}Pu , respectively), causing heat and neutron release to increase after millennia.

years for α emitters with negligible spontaneous fission shares, radiotoxicity (i.e., the effects caused by particles of ionizing radiation emitted during decay) prevails even against this chemotoxicity. Among these nuclides, $^{239,240}\text{Pu}$ (which are produced together in a reactor given there is substantial irradiation of a uranium sample) are peculiar in their radiotoxicity although being rather long-lived as they do enrich in the body at very sensitive points: the marrow and mucosa around or in bones, and liver, while radioactive (“hot”) particles may be inhaled and reside in the lung, exposing it to radiation.⁸⁸⁾ This compromises sensitive tissues.

Cancer rates, for example, bone skin sarcomas and their metastases, will thus increase after a Super-GAU (German: *größter anzunehmender Unfall*, meaning worst case, meltdown) if plutonium is released, like in the 1951 Mayak accident (Russian Federation) or after a Pu-based nuclear fission bomb was destroyed in: (i) an airplane crash at Thule (Greenland) in 1968 or (ii) by mis-ignition (“fizzle”) in the *Hardtack Quince* test (explosion yield only 0.02 kt TNT) at Runit Island, Enewetak Atoll (now some part of the Republic of Marshall Islands) in 1958. Both latter events spread several kilograms each of ^{239}Pu over a very restricted area which yet proved impossible to clean effectively,⁸⁹⁾ which is the gravest possible kind of catastrophe from an ecological and ecotoxicological point of view, going beyond even what happened around either Fukushima or Chernobyl: then the environment is so polluted, including groundwater, that access is strongly impeded for centuries or even longer.

As with Chernobyl and the Bikini Atoll test site, the animals and plants apparently adapted to the harsh radiological conditions there. Starting soon after the Chernobyl accident, researchers noted diverse animals (and some humans) returned to the off-limits area around Chernobyl, including the so-called Red Forest and the decontamination lake, such as wolves, foxes, lynx, mooses, hares and many kinds of birds. Among these, there are species which try to avoid man,

88) Note that some 6 t (!) of ^{239}Pu which escaped fission during nuclear bomb tests were spread upwards into the stratosphere as an aerosol which still keeps on being deposited (“fallout”), besides some other transuranic nuclides: from analyses of fallout composition, 1100 kg of ^{240}Pu , and substantial amounts of $^{241,243}\text{Am}$ (produced in nuclear weapons containing ^{241}Pu or ^{242}Am as fissionable nuclides which have much smaller critical masses with fast neutrons than all $^{233,235}\text{U}$, and ^{239}Pu) are determined. Estimated amounts of the latter are 25 kg ^{241}Pu , 70 kg of its decay daughter ^{241}Am , and 2.5 kg ^{238}Pu (most of it from break-up of a RIG during re-entry in a 1960s space probe mission; data calculated from Breban *et al.*, 2003). Besides this there are natural contributions of plutonium in the biosphere: some 5 kg of ^{244}Pu is still left over from the origins of

the solar system owing to its 83 mio. year half-life, and trace amounts (<1 g) ^{238}Pu from the double-beta decay branch of ^{238}U . Most fallout radioactivity is still due to ^{241}Pu ($T_{1/2} = 14$ year) but this is less destructive in radiotoxicological terms because it undergoes β^- - rather than α -decay, followed by each comparable activity of $^{239,240}\text{Pu}$ and ^{241}Am ($T_{1/2} = 433$ years).

89) Probably this list should include the doubtful results of (2 out of 5) nuclear bomb tests in Pakistan (1998) and the first one in North Korea (2006), neither yet precluding a burst of Pu and fission products to the surface though these were underground test “fizzles”. Runit Island (Pacific Ocean) now is used as a dump site for highly contaminated materials from nearby test craters, the whole capped by a concrete dome of some 100 m diameter.

prompting them to invade an area where there are (almost) no humans left behind. In addition, biodiversity is lower than in comparable areas, brain sizes tend to be reduced in both mammals and birds; and there are other malformations, tumors and evidence of genetic alterations (Gill, 2010). Likewise, there are lots of aquatic life in Bikini Atoll [except for the crater basin of the largest ever United States test *Castle Bravo* (1954, some 15 MT)] but once again there is reduced biodiversity.

At least since 9/11 some ten years ago, but actually ever since the first threat to attack a NPP by a flying passenger airplane abducted before (in 1972 over Oak Ridge, Tenn., USA), this has concerned the citizens and public authorities of countries which make use of nuclear fission power. While older NPPs—all over the world—must be considered to be improperly protected against even the impact of a smaller airliner, there is virtually none anywhere to withstand the perpendicular impact of a fighter plane.⁹⁰⁾ In addition, global warming and eutrophication combine to increase the likelihood that river or ocean water cooling can no longer be taken for granted in summer at least: already in 2003, rivers became so warm all over central Europe, probably related to global warming, that NPPs from France to Lithuania had to be shut down for many weeks. In the same summer, cooling water entries at the Russian Sosnovy Bor plant were blocked by algae excessively growing in the adjacent Bight of Helsinki. Either problem is likely to occur more often in the future.

Transmutation (Etspüler, 2011; De Bruyn, 2009) is discussed as a means of faster disposal of fissiogenic radionuclides, by exposing the nuclide mixture obtained by fuel reprocessing to a high-energy proton beam. Fission products which are distinguished by a considerable excess of neutrons in their nuclei hence are brought closer to stability while actinoides will either undergo fission directly or produce at least nuclides of much shorter lifetimes. It is completely unsettled and doubtful whether this can be done on a scale of tonnes of material.

4.4.2

Rethinking to the Way for Ecological Economics

The previous section was mainly concerned with the problems of conventional and nuclear energy sources from all economic, ecological and political points of view, which are going to challenge us more and more in the near future. There are several quite different—and mutually independent—reasons to switch to alternative, that is, regenerative resources of energy, including resources of fossil fuels becoming scarce(r), constraining greenhouse gas emissions and striving for geopolitical risk management (spreading suppliers among most diverse regions and political systems, if you are not in a position to produce the materials related to your energy demands domestically). Although there are numerous incentives, this transformation will take several decades not only on a global scale but also in

90) The jet engine compressor axle in a military plane is about 3.0–3.5 m long, made of dense metals like niobium alloys, then hitting a concrete ($\rho \approx 2.8 \text{ g/cm}^3$) shell

at about the speed of sound. This will suffice to penetrate some 10 m (!) of concrete, as compared to an actual containment thickness of <2 m.

national dimensions, and it depends on both economic interest positions and technical innovations. While wind energy is technically “ripe” now, the size of rotors is no longer limited by mechanical problems with generators and so on exposed to vibrations and bending along a horizontal axis, but by the size of available cranes required to erect them (maximum: some 200 m rotor diameter, 7–9 MW peak power). Also, photovoltaic devices reasonably benefit from the technologies of semiconductor processing—which is now advanced much beyond anything which would ever be required in solar energy conversion—becoming a large-scale business also [the combined area of highly integrated chips which make it to the markets in computers and lots of devices (some 70 of them alone in a common car) is in the km²/year region]. However, extracting energy from the oceans currently takes an engineer’s ingenuity still to make it reasonably work. For solar energy, the “surviving” technical innovation challenges are restricted to thin-layer and organic semiconductor systems and to conversion/storage in a convenient chemical storage form, like methanol.

The following part of this chapter will deal with both those energy forms already present on the global market for energy conversion devices, plus a discussion of how energy can be harvested from the open sea, keeping in mind which will be the challenges for Germany or Italy who both decided either to abandon the use of nuclear energy until 2022 (Germany) or not to re-start it (Italy). This prompts the question whether redesigning the energy supply of a medium-sized highly industrialized country, whose consumers are really demanding, within some ten years, merits further consideration.

4.4.2.1 Global View of Renewable Energy

Available energy resources are “renewable” when they are sustainable and environmentally benign (which need not coincide) if:

- They renew themselves either in the short term by itself (e.g., biomass);
- Their use does not contribute to the depletion of the source (e.g., wind, sun, water).
- They do not contribute to an impact on the environment.

Sustainability in that sense means a triad related to ecology, economy and social affairs. Figure 4.44 gives an overview of different energy sources like sun, wind, water, geothermal energy and biomass for the establishment of technical supported renewable energies.

In 2010 the Renewable Energy Policy Network for the 21st Century (REN 21) published the Global Status Report on Renewable Energies (REN 21, 2010), parts of which are now to be quoted. In its preface, El Ashry noted that already more than 100 states have political agendas or strategies in 2010 in favor of spreading and widening uses of renewable energy sources, about a doubling from just 55 states five years before (El-Ashry, 2010). In 2009, largest increases were observed with wind power and photovoltaics, investing some US\$ 150 bio. into extending capacities, producing and implementing renewable energies versus but US\$ 30 bio. in 2004. Except sometimes for advancement of nuclear energy, more money is

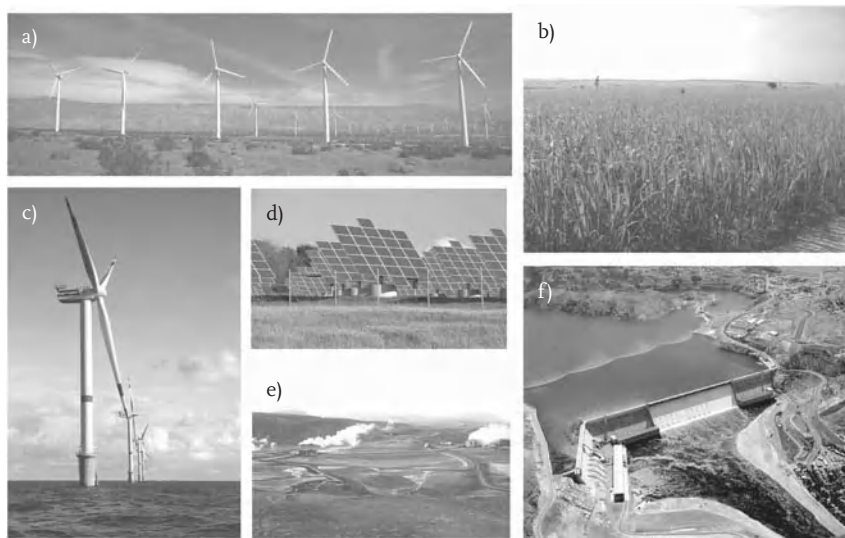


Figure 4.44 Renewable energy sources: onshore and offshore wind power, biomass, solar power, geothermal, hydropower. (a) Onshore wind turbines located outside Palm Springs (Calif., USA; photography: wikipedia, Tim1337). (b) Sugar cane is a major supplier of biomass, which is used either as food or energy supplier (photography: wikipedia, Culture sugar cane, Avaré, São Paulo, José Reynaldo da Fonseca, 2006). (c) Newly constructed offshore windmills on the Thornton Bank, 28 km off shore, on the Belgian part of the North Sea (photography:

wikipedia, Hans Hillewaert, 2008). (d) Photovoltaic array near Freiberg (Germany; photography: wikipedia, I, Eclipse.sx). (e) Krafla Geothermal Station in 2006, North Iceland (photography: wikipedia, Mike Schiraldi). (f) Grand Coulee Dam is a hydroelectric gravity dam on the Columbia River (Wash., USA). It is the largest electric power-producing facility in the United States (photography: wikipedia,* U.S. Bureau of Reclamation). Larger dams are located in Russia, Brazil and China.

allocated into capacities and growth of renewable energy sources than into fossil ones. By reaching substantial shares of energy input (particularly in some less-populated countries like Denmark, Latvia or Mongolia), renewable energies did access a turning-point which renders them significant also addressing the problems of climate change. As implied before, acceptance and broad application of renewables are not (no longer) restricted to highly developed industrialized countries but extend to developing nations now displaying more than half of implemented and operating renewable energy supply systems.⁹¹⁾

91) However, it remains to be seen how far this is actually in favor of domestic development and better situations especially in rural areas or larger autonomy toward globalized oil and coal markets or is another blueprint for the export of goods to the North: growing sugar cane and oil palms for biofuel exports in Brazil or Indonesia threatens

local primary forests if not even the food supply there. The Desertec blueprint (www.desertec.org) for producing lots of hydrogen from solar sources in northern Africa revives existing supplier roles with countries like Algeria once again.

* <http://users.owt.com/chubbard/gcdam/html/photos/exterior.html>

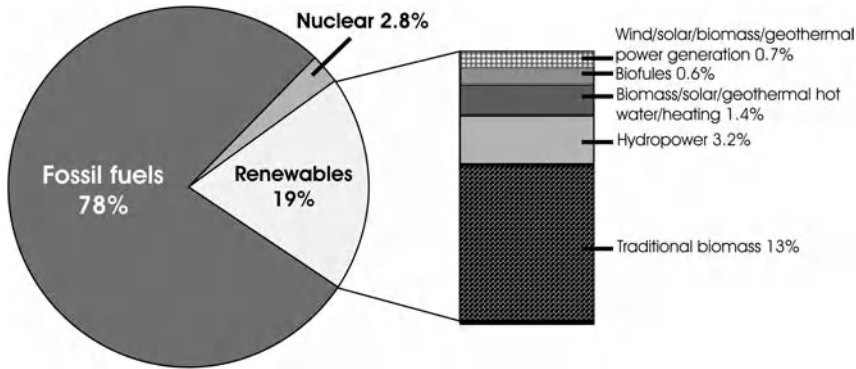


Figure 4.45 Global final energy consumption of conventional and renewable energy in 2008, after REN 21 (2010). Also consider footnote 92.

Figure 4.45 gives a more precise idea of present relevance of renewable, their share being some 19% of total in 2008,⁹²⁾ including all traditional sources of biomass energy carriers (biogas, ethanol, wood, etc.), large hydropower plants and the “novel” kinds of renewable like small-scale hydropower plants, modern biomass sources, wind and solar energy, geothermics and biofuels.⁹³⁾ Most of these 19% (13%, that is, a relative 70% among the renewables) rests with traditional biomass used for cooking and heating. This, however, is subject to some change and even cutbacks, especially because there is virtually no possible firewood (not even small branches) left around megacities (i.e., up to 50–70 km from the outer edge of “informal suburban settlements”!) all over the developing and threshold countries, causing firewood to be replaced with more advanced devices (e.g., solar cooking) or at least a more efficient use of these resources. Hydropower represents 3.2% (17% out of renewables) and is growing modestly but from an already advanced level. The other renewable energies contribute 2.7% (relative share: some 14%) and are undergoing very fast growth in both industrialized and certain developing countries.

In developing countries, renewable energies have a particular role also in national support and corresponding policies, which contributes to their present share of renewable energy capacities of more than 50% [but compare this to both their share of global population, which (including the BRIC States—Brazil, Russia, India, China—except Russia) is >80%, on the one hand, and their share of global energy consumption, on the other hand]. China now leads in several indicators of

92) Share of final energy means: at the point of end use, such as electricity, heat and directly used fuels. This method counts all forms of electricity equally, regardless of origin. The European Commission (EC) adopted this method in 2007 when setting the European Union target of a 20% renewables share of energy by 2020. Thus, it could be called the “EC method” (REN

21, 2008), page 21; available at www.ren21.net.

93) To be exact, it should be noted that some of the “modern” ones actually are rather old, from small-scale water mills which also deliver electricity, up to biofuels [Rudolf Diesel already demonstrated his engine running with peanut oil fuel at the 1900 World Fair (EXPO) in Paris].

market growth. Among the suppliers of wind energy, India now ranks fifth globally and is doing substantial expansion of biogas and photovoltaic capacities, especially in the countryside (but it also plans to install another 15 NPPs owing to its being populated as densely as, e.g., Belgium or the Netherlands in total, and citing growing industrial energy demands). Brazil now is the key supplier in ethanol from sugar cane, adding to other kinds of biomass and windpower in her renewable energy portfolio. Concerning the complete array of renewable energy sources, Argentina, Costa Rica, Egypt, Indonesia, Kenya, Tanzania, Thailand, Tunisia, Uruguay and others boast high growth rates, often even surpassing their sometimes impressive gross economic growth rates.

To put it in a nutshell, the geographical distribution and political significance of renewable energies has altered considerably in favor of almost global distribution and application. As compared to quite few countries in the 1990s, there are at least 82 countries now operating wind power plants. As for manufacturing these devices, production was relocated from Europe to Asia, with the largest shares in China, India and South Korea, which additionally become more devoted to renewable energy applications. China is not only the “production yard” of the world for conventional items including consumer electronics, but in 2009 made 40% of PV devices (from solar cells to complete panels with control and DC/AC converter units), 30% of the world’s wind power plants and even 77% of solar-driven water-heating collectors. All over Latin America states like Argentina, Brazil, Colombia, Ecuador and Peru are increasing their production, including exports of biofuels, additionally investing in other kinds and technologies of renewable energies. More than 20 countries in the “Solar Belt” of middle, northern and sub-Saharan Africa are involved in renewable energy markets.

Large economic gains and considerable further technological changes are also to be achieved from this state of affairs and developments, beyond the principal actors of the highly developed world like the European Union, United States, Australia, Canada or Japan. With renewable energies getting a truly global footage and application area, there is internationally growing confidence into renewable energies being less susceptible toward perturbations by either political turnovers or market changes such as financial crises than “classical” energy carriers (which readily, like other raw materials, become an item of speculation undergoing tremendous price level oscillations in such conditions).

Another impetus to renewable energy development—as to every other kind of large-scale technical innovation—is its inherent potential to create entire new industries⁹⁴⁾ and thus millions of new workplaces. The latter fact is, by the way, the positive, friendly side of the “dual-use” problem: both engineers and blue-collar

94) Or at least create vast uncharted fields of opportunities for existing technical branches: in photovoltaics, much larger amounts of semiconductor-grade to medium purity, silicon, SiH₄ and GaAs are used than in integrated (chip) solid-state microelectronics (e.g., GaAs chips are

applied in cellphones), whereas technologies required to obtain control of a large rotating propeller in changing conditions, originally developed for helicopters, now increase reliability and output of wind-power systems.

technicians who were so far mainly concerned with development and production of arms systems had to strive to save and “humanize” their workplaces after the Cold War came to a unanticipatedly happy end around 1990. These highly skilled metal workers and engineers at Kiel harbor (Germany) then focused on wind power plants (with rotor techniques borrowed from military helicopters) and integrated current-heat support systems (using Diesel engines originally designed for tank propulsion to consume and convert plant and waste oils to produce some 1 MW each of electricity and heat). So, although not creating environmentally benign branches from scratch, this “*Arbeitskreis für alternative Produktion*” (Work-group planning for alternative production) and similar endeavors in the United States, United Kingdom, Australian and French arms enterprises effectively increased the array of possible customers much beyond the state (i.e., department of defense and sometimes police forces) and in the same turn reduced political–military dependences, even though most of the respective employers did not really like the idea of employees considering what should (better) be produced on their own . . .

This is part of the ethical issues and bonuses associated with alternative energy production: there is a considerable bonus in terms of both workplace safety and numbers of workers require to install and run 1 GW_{el} of alternative energies as compared to fossil and nuclear ones; besides there are fewer risks associated with making PV devices than with coal or uranium mining for the miners themselves, counting and comparing, for example, mine accident or cancer fatalities per MWyear. In 2009, there were an estimated three million workforce directly related and devoted to renewable energies, about half of them concerned with biofuels and many more than this in branches indirectly entangled with renewables (Table 4.7).

What are the recent performances of renewable energies as of 2009 (Figure 4.46; source: REN 21, 2010)? For the second consecutive year, in 2009 in both the United States and European Union the newly installed renewable energy capacities exceeded those of combined conventional fossil energies and nuclear power. Renewables accounted for 60% of newly installed power capacity in Europe in 2009, and nearly 20% of annual power production.

Christopher Flavin (Worldwatch Institute), pointed out in his paper “*Renewable Energy at the Tipping Point*” within the REN 21 report for 2010 (REN 21, 2010) that China’s recent leader role in producing wind rotors and photovoltaic devices just gives proof of the political prerogatives in favor of renewable energy exploitation, including both laws and funding to be successful. Although there were initial problems, the important reforms in China starting with the national legislation on renewable energies of 2005 caused fast and efficient development there. China since then increased her efforts trying to become a leading innovative power as well as key producer of renewable energy technologies.

Table 4.8 gives the five countries which are the most important players concerning renewable energies, as of 2009.

Owing to the well-known variabilities of renewable energy output which are due to weather, daytime and longer-period (tidal power plants) periodic or aperiodic

Table 4.7 Jobs worldwide from renewable energy (REN 21, 2010 with added information from the United Nations Environment Program Report 2008).

Industry	Estimated jobs worldwide	Selected national estimates
Biofuels	>1 500 000	Brazil 730 000 for sugar cane and ethanol production
Wind power	>500 000	Germany 100 000, United States 85 000, Spain 42 000, Denmark 22 000, India 10 000
Solar hot water	~300 000	China 250 000
Solar PV	~300 000	Germany 70 000, Spain 26 000, United States 7 000
Biomass power	–	Germany 110 000, United States 66 000, Spain 5 000
Hydropower	–	Europe 20 000, United States 8 000, Spain 7 000
Geothermal	–	Germany 9 000, United States 9 000
Solar thermal power	~2000	Spain 1000, United States 1000
Total	>3 000 000	

Further information about the evaluation of the data is provided in REN 21 (2010), page 75, note 226. The table is incomplete.

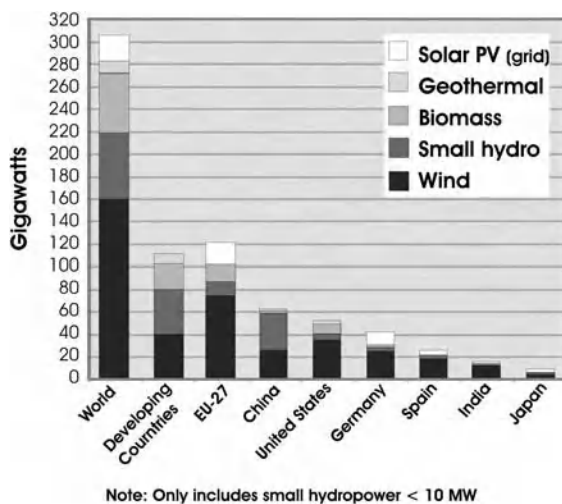
**Figure 4.46** Renewable power capacities in 2009 (without the inclusion of large-scale hydropower) for: the developing world, the European Union (EU-27) and the top six countries (REN 21, 2010).

Table 4.8 The five countries which are the most important players concerning renewable energies (as of 2009; REN 21, 2010).

Top five ranking	1	2	3	4	5
Annual amounts in 2009					
New capacity investment	Germany	China	United States	Italy	Spain
Wind power added	China	United States	Spain	Germany	India
Solar PV added (grid-connected)	Germany	Italy	Japan	United States	Czech Republic
Ethanol production	United States	Brazil	China	Canada	France
Biodiesel production	France/Germany		United States	Brazil	Argentina
Existing capacity at end 2009					
Renewables power capacity (including only small hydro)	China	United States	Germany	Spain	India
Renewables power capacity (including all hydro)	China	United States	Canada	Brazil	Japan
Wind power	United States	China	Germany	Spain	India
Biomass power	United States	Brazil	Germany	China	Sweden
Geothermal power	United States	Philippines	Indonesia	Mexico	Italy
Solar PV (grid-connected)	Germany	Spain	Japan	United States	Italy

changes, there are much larger theoretical (peak power output) renewable energy technical potentials than average yields. The present (as of end of 2009) capacity of a global 1.23 TW (1230 GW) which now constitutes just over 25% of total electric generating capacity worldwide thus is considerably larger than the actual share/contribution of produced electricity.

What about Ocean-related Energy (Waves, Ocean Currents, Tidal Power Plants, Osmotic Energy Conversion, Ocean Thermal Energy Conversion)? The power associated with flowing water is impressive and motivated people to use it many centuries ago in mills located at running creeks and rivers. It was an obvious idea to extend this technique to tapping ocean currents, like the Gulf current, as well as tidal water flows which can reach speeds much above those seen in most rivers [e.g., some 6 m/s (11 knots/h) along the Welsh coast of the Atlantic ocean (rather than perpendicular to it)], providing concentrated energy as flow speeds are close to those in air (wind), with water being 800 times as dense, thus a rotor of equal diameter exposed to a water flow of equal speed delivers 800 times as much power [or the same power at $\sqrt[3]{1/800}$ this speed, i.e., some 10.8%]. Basins which are filled with water at maximum level differences of a few meters are commonplace



Figure 4.47 Aerial photograph of the world's biggest tidal power station. The Rance tidal power station is located at La Rance (northwestern France) in the mouth of the River Rance, next to famous island Mont St. Michel (photography: wikipedia).

in electric storage (in German: *Pumpspeicherwerk*), with the same being offered by tidal changes of ocean and estuary water levels [the largest tides are seen in river mouths, for example, River Severn (Wales) or River Rance (France, Normandy) at some 10m], and not just after pumping water into them by electrical power obtained otherwise, but for free twice a day (actually even four times daily using differences of either levels) . . .

Concerning periodical filling and uncharging of storage basins connected to flowing water turbines, there is still but one large power plant (240MW_{el}) in the world, connected to the French grid back in 1967. It is located at La Rance in the mouth of the River Rance, next to the famous island Mont St. Michel (Figure 4.47).

Here, the tidal water level differences are far larger than the about 3.5 m of global average (isolated ocean basins, like the Black and Baltic Seas, and even the Mediterranean Sea, tend to lack any significant tides; e.g., average tides in Baltic sea are some 20cm); the minimum tidal heights required for meaningful operation of a tidal power plant are estimated to be some 5 m (Hoffmann, 1990). Obviously the gain of energy from a basin of given size interacting with the tide flows increases by the *square* of tidal water level changes: the amount of water flowing in and out is proportional to tidal height, and so is the energy gain from a given mass of water flowing through the turbines. Now being operated for more than 40 years (it was connected to the French grid in 1967), effects from this plant and its overall performance can be well evaluated:

- Local tidal height decreased from some 14 (!) to <8m due to deposition and relocation of sediments.

- Corrosion is an issue, requiring both to avoid combination of different alloys in the construction to exclude galvanic effects in seawater, and active electrochemical protection measures.
- There were some ecological by-effects concerning distributions of limnetic and marine fishes in and on either side of the basin, with the power plant shifting the limits of marine and limnetic populations of fishes somewhat downstream into the estuary. The turbines rotate so slowly that both fishes and squids can pass them without being hurt, much unlike classical running-water power plants.
- Actual average output to the grid is some 540 GWh/year, that is an average 62 MW, about 25% of nominal power production.

Nevertheless, the La Rance plant remains unique in the world, being still the only large-scale plant, although sites having even higher tidal heights such as Bay of Fundy (Canada, up to 19 m) have been used for yet smaller installations.

Waves may be destructive but their energy can also be technically exploited, for example, with transducers based on either bending of some part of the device (hydraulically or by piezoelectric⁹⁵) devices). Other devices employ either systems operating on periodically compressing and expanding air by by-passing volumes in a volume (some hollow metal or concrete bunker) under which the waves pass through and pass this air over a rotating turbine or using the alternating flow directions of water or directly converting the water level oscillation into electricity by electromagnetic induction.

It is estimated that one can gain some $15 \text{ kW}_{\text{el}}$ (130 000 kWh/year) from a single meter of coastline around the North Sea which is comparable to the gain earned by covering about *one km* of land behind this shoreline by photovoltaics in the same climate (this sounds stunning if not paradoxical but consider the width of the seas where the waves could gain energy before from wind rather efficiently converting solar energy). So far, wave energy converters were constructed at Western ocean coasts in the northern hemisphere, including south west Norway (Toftestallen, near Bergen), the northernmost Scottish coast, open to the Atlantic Ocean, and Oregon. A most straightforward way to convert mechanical movements into electricity, besides of piezoelectric techniques, is the following one: magnetic induction. A buoy is towed to the seafloor, with a magnetic shaft tethered to it while the floating part of the buoy contains some induction coil which hence moves up and down around the shaft within the magnetic field produced by the latter, directly producing an alternating current even though its voltage and frequency still have to be adjusted.

Of course such interferences with natural water flows may alter and affect the ecological situation in estuaries especially; in the best cases, using both tidal and wave energy reduce coastal erosion.

Less obvious sources of energy associated with ocean and shoreline, respectively, include the *temperature difference* between surface waters and the deep sea

95) Piezoelectricity means electricity resulting from applying pressure, squeezing.

(particularly in the tropics, except for the Red Sea and its annexes like Gulf of Aqaba/Eilat), some 25–30°C there,⁹⁶⁾ and the *gradient in salt content*, and thus, osmotic pressure⁹⁷⁾ difference of some 26 bar between the ocean and freshwater from rivers, creeks running into it (the latter being identical to having this water falling through a Pelton turbine from a height of about 260 m). Before dreaming of what the latter source could deliver when passing a substantial part of the freshwater flows of giant rivers like the Amazon, Mississippi, Yangtsekiang (China's largest river), Congo or Siberian rivers like the Yenisei through such devices, one should be reminded of some problems which are not yet solved. The only demonstration plant existing so far is located at a creek which empties into a fjord in Norway, producing some 3–4 kW of electric power since November, 2009. There are three quite different kinds of converting osmotic potentials into electricity:

- Using a water-permeable yet pressure-proof membrane (this is done in Norway). The saltwater content of this closed membrane volume is going to absorb pure water from the freshwater passed along outside (i.e., in the mouth of the river). Due to the osmotic pressure, the water level inside will increase considerably, allowing to pass it over a falling-water turbine and produce electricity eventually. This process is a somewhat periodical one: as the saltwater gets diluted during the process, you need to discard it into the ocean sooner or later and re-fill the chamber with “pure” (3.5% salt) ocean water. By now, electric power output is about 1 W/m² of membrane interface area, trying to achieve 5 W/m² soon.
- Electrochemical settings using the diffusion potential: concentration differences leveled off by diffusion create electric potentials even though no redox reactions are involved in charge transfer. Likewise, second-type electrochemical

96) At a surface temperature of some 300–305 K in tropical waters, the Carnot (most efficient heat engine) maximum efficiency would be about 8–10%. Usually in OTEC plants ammonia is used as heat transferring working medium; actual efficiencies are about 3% due to long hoses required to exchange hot and cold waters. Rather than steep cliffs selected earlier, OTEC plants are now located on either ships or floating constructions much like those employed in crude oil production. Given the problems associated with coral bleaching due to surface waters exceeding 30°C, some larger use of the OTEC technology should even provide a real ecological bonus while mixing nutrients between deep and surface waters might cause problems of eutrophication.

97) The osmotic pressure of some solution is about the pressure which would be exerted

if the same concentration of dissolved entities (i.e., ions from, say, MgCl₂ solutions, to be counted individually, hence producing three times the osmotic pressure in water or acetonitrile than if dissolved in non-ionizing solvent like a long-chain alcohol). 1 M/kg of solvent (here: water) hence is equivalent to a gas compressed to 1 M/l which is tantamount to a pressure of some 24 bar at 20°C. A unimolar MgCl₂ solution in water would thus produce an osmotic pressure of more than 70 bar, while the corresponding value for seawater—which is 0.55 M NaCl solution to a first approximation—is about 26 bar (the actual value for Norway is a little smaller because of: (i) the water being colder and (ii) some dilution by the very freshwater discharges into the Fjord site used which is rather remote from the open ocean).

cells draw upon concentration potentials: an electrode made of combined silver and AgCl (both solid and mixed among each other) will adjust its potential according to the concentration level of chloride ions. This can be used both in analytical chemistry and for producing electric currents from chloride solutions which differ in concentration (freshwater typical values being 1–2 mM/l as opposed to 0.55 M/l in seawater, giving an open-cell voltage of 150–170 mV).

- Theoretically speaking, the zeta (electrokinetic) potential could also be used in osmotic energy conversion: by osmotic pressure differences forcing water through some membrane, or a column filled with a packed solid, it will produce an electrical potential difference between either side of the interface. This potential is due to selective adsorption of cat- or anions onto a typically charged particle, charging being caused by oxide/hydroxide particles (say, wet alumina) behaving as an acid (adsorbing hydroxide) or base (adsorbing protons) depending on local pH, co-sorbents and material (point of zero zeta potential). Then the other, non-adsorbed ions will be passed through along the solvent, and a potential of typically half a V forms. The effect is reversible (electrokinetic water pumping).

The problems are with membrane stability or, more generally, also affecting electrochemical systems, clogging of the interfaces by biomass (mainly phytoplankton) or even mineral concretions. The Norwegian success terminated a history of decades of failing experiments on osmotic power production, indeed.

Things are a little different—and better, rather more advanced—for *ocean thermal energy conversion* OTEC: the first plant ever of this kind was constructed by French Georges Claude (1870–1960) at the coast of Cuba already back in the late nineteenth century. OTEC devices are simple thermal power plants using rather small T differences, more like a steam engine than comparable to turbines, coal-fired plants or internal combustion engines.

The global distribution of chances for this way of harvesting solar energy indirectly (having hot water from insolation in the tropics while cooling is provided by Arctic or Antarctic undercurrents at some 1000–2000 m of depth).

Eventually, there can be integrated offshore energy parks making use of almost all the energy sources discussed above combined on, or beneath, a tethered floating island.

For heating purposes, *geothermal energy* has been well-established for many decades in countries like Iceland, New Zealand and several developing countries in Central America, such as El Salvador. Although electrical uses, with geothermal (fumarole) vapors directly run through a steam turbine, were first tried in Italy more than a century ago (at Larderello in 1904, delivering about 200 W), corrosion and clogging problems remain severe until this day. The obvious reason is the “contamination” of fumaroles with both clogging agents like boric acid and hydrolyzable volatile metal chlorides, besides large shares of corrosive gaseous acid precursors like SO_2 , HCl and HF . So one has to create a primary heat exchange cycle directly exposed to these corrosive items and a secondary one linked to the

heat/mechanical/electrical conversion systems, much like in nuclear power plants and mainly for the same reasons (if not even worse here), and worse due to the rather small heat difference, this decreases total efficiency of conversion. When obtaining the vapor from underground wells drilled several kilometers into the Earth's crust rather than operating close to active volcanoes, the clogging of drilling holes or rock fractures required to circulate some operating medium also remains critical. So it is safe to predict that geothermics will remain more concerned with heating (houses, swimming pools, etc.) than with electricity production in the near future.

4.4.2.2 Renewable Energy in Germany and the Planned Nuclear Exit

Concerning her gross domestic product (GDP), Germany is the largest national economy in Europe and fourth in the world. In 2009 she was second in export and third in import values. Like with the GDP, Germany ranks fourth in energy consumption [measured in fossil fuel (hard coal) mass equivalents (British thermal units: BTUs)] but is just 21st among the energy producers in the world (U.S. Energy Information Administration, 2008). The intention of the Federal Government of Germany in fulfilment of Kyoto Protocol obligations is a reduction of green house gas production until 2020 about 40% and until 2050 of up to about 80–95%. Quite recently, the greenhouse gas issue and the risk of nuclear power plants (Fukushima disaster in 2011) were aggravated by the decision to abandon nuclear energy use in Germany in the early 2020s. Figure 4.48 shows the fuel mix in 2010 and the aimed fuel mix in 2050 in Germany that mainly will be supplied by wind and solar power.

By steadily replacing fossil energy sources with renewables, the share of the latter will increase even allowing for a slight increase of energy consumption (which in Germany, like most other highly developed countries, is rather constant

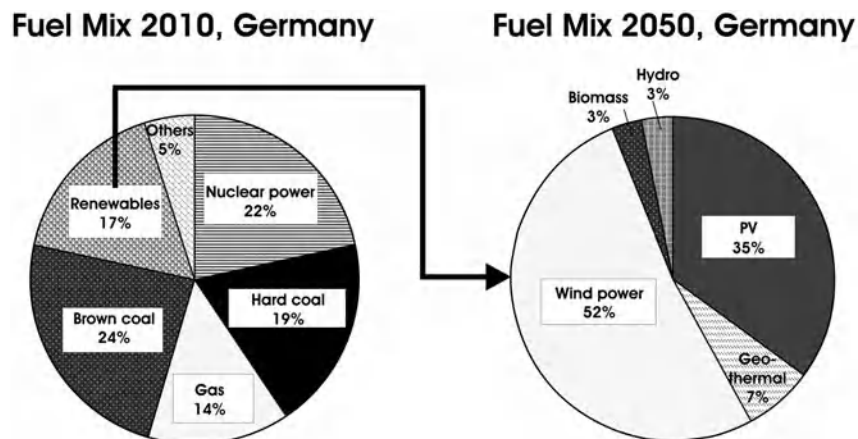


Figure 4.48 Energy mix contributions in Germany in 2010 and the probable future in 2050 (Burkhardt and Weigand, 2011).

for decades now, notwithstanding a slight decrease in population to become faster soon). Hydropower is fully established now except for reactivation of very small local plants many of which had been in operation since the early twentieth century until recently. So the 3% share of today is going to remain almost equal. 35% from photovoltaics correspond to an average output of some 23 GW, which in our climates is tantamount to an introduced peak power of 130–150 GW, more than twice that what now is funneled into the entire grid by all kinds of power plants. It remains to be figured out how to deal with this excess energy on sunny summer afternoons, possibly by chemical storage (water electrolysis, then linked to fuel cells). The total area required to produce this amount of PV electricity is about 1000 km² [less than 0.3% of Germany's total area (356 000 km²) and <10% of the fields on which “energy plants” are now grown (>12 000 km² are covered with rape alone)], even assuming no further improvement of today's Si hydride polycrystalline or CuIn(S; Se)₂ thin-layer solar cells (some 13% efficiency).

4.4.2.3 The Growth Region Ems Axis, Lower Saxony (Northwestern Germany)

The previous sections dealt with the global-scale relevance of renewable energies. Besides the environmental issue, there are both economic and social surpluses produced by creating novel workplaces.

This can turn what was formerly “just” an agrarian region into a diversified boom area, as will be shown by the example of the so-called River Ems Axis (Lower Saxony, northwestern Germany). For more than a decade now the region has kept increasing its workforce by 3% per year—no “Mc jobs” but fully qualified jobs which produce social security and modest earnings, with >10 000 enterprises which keep expanding and creating new jobs year after year. The regional motto reads: “Powerful, innovative and ready to achieve by unconventional solutions—these are our region's benchmarks.”

As the Emsland Axis is located next to the North Sea, maritime-related activities are prominent with shipyards, shipping companies, and windpower plant producers locating here, among suppliers of other renewable energies. This model region was created by a combination of prudent political support, improvement of infrastructures, a synergy among regionally active enterprises and finally the support of the public. It is located near the Dutch border in central Europe, making use of the already existing East–West connections, in addition linking the North Sea shores to the German megalopolis Ruhr district, which is the most populated part of the most populated and economically prolific *Bundesland* of Germany. The Ems Axis includes the counties Wittmund, Aurich, Leer, Emsland, Grafschaft Bentheim and Emden City with her large harbor (see Figure 4.49).

There are six permanent workgroups concerned with energy, integrated maritime economy, tourism, production of plastics items, vehicles and machines, and finally logistics to initiate and run projects. It is the aim of these workgroups and the economic region to make the Ems Axis an independent axis along which economic and travel, transport activities will be organized. This implies a strengthening economy-related infrastructure and creating networks for the regional economy.

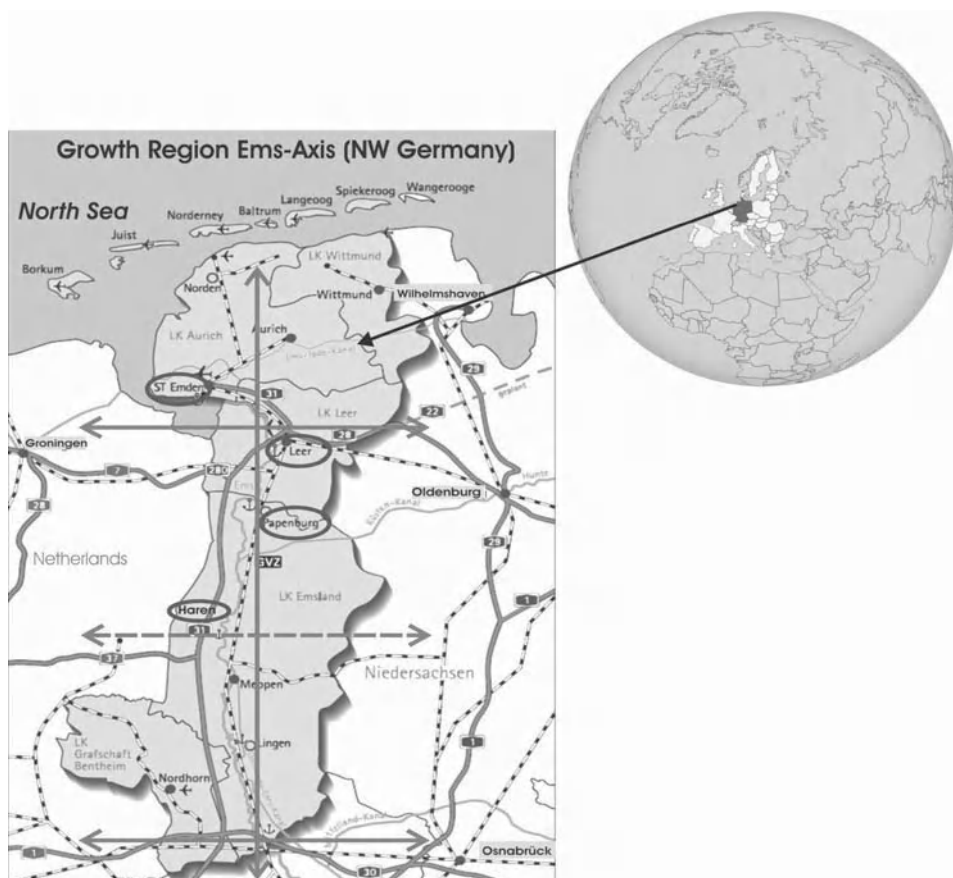


Figure 4.49 The growth region Ems-Axis in northwestern Germany. This figure shows the excellent infrastructure which will imminently cause new enterprises to settle and expand here. The East–West and South–North highways (motorways) with the No. 7, 28, 30, 31 and 37, while rivers and channels for shiptravel are marked medium gray. These are the River Ems, which is deep and wide enough to permit economically meaningful transportation by ship, and the Dortmund–Ems channel, which extends almost parallel to it. Railway tracks are outlined in black and white. Framed: the cities of Leer and Haren (Ems) are among the most important locations for shipowners all over Germany. In

Papenburg there is the Meyer shipyards, among the largest in Europe and moreover the one producing the biggest ships (passenger and cruise ships). Other notable shipyards located next to the shore at Emden recently rather switched to producing windpower plants. The Ems Axis is distinguished by intense economic activities covering all energy supply, integrated maritime activities, agriculture, tourism, processing plastics, metals, building vehicles and machines and providing logistical infrastructure. The main figure of the Ems Axis is modified after www.emsachse.de. The figure on the right is from: wikipedia, TUBS.

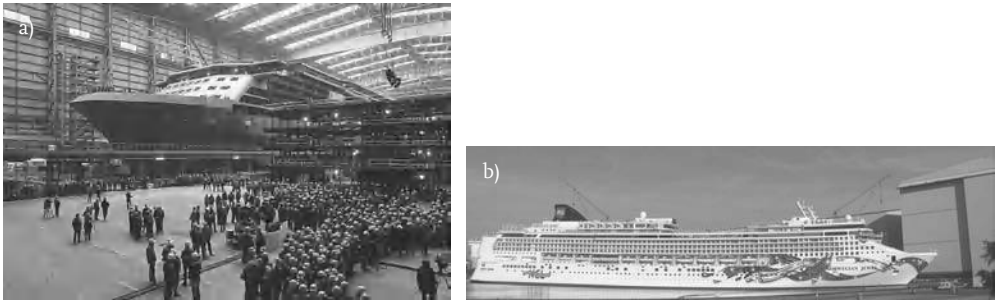


Figure 4.50 Meyer shipyards at Papenburg (northwestern Germany). (a) The largest dock is an incredible 504 m long. (b) Norwegian Jewel in front of the 70 m tall Meyerwerft Hall. Photos courtesy of wikipedia: (a) C. Walther; (b) satermedia.de, C. Brinkmann.

The cities Haren and Leer combine to be the second-largest shipowner's site in Germany. A total of 750 ships are run from here, making these two little towns special and significant players in running shiptravel and dockyards and providing additional maritime goods and items, together with Papenburg. The existing travel infrastructure allows the processing of materials inshore and, using local logistics, building huge ocean liners like that for the Disney Cruise Line (340 m long and 37 m wide, 128 000 t, scheduled to accommodate some 2500 passengers) at Papenburg's Meyer dockyards (Figure 4.50). The latter commands the globally most advanced instrumentation and facilities for building ships, its workforce being about 2500.

One should mention that there is minimal required bureaucracy used to get these infrastructures. This enabled Motorway 31—a crucial North–South connection—to be completed years ahead of planning, with the region providing the required funds itself by joint and coordinated action. Another ambitious project was Euroharbour Emsland at Haren (operated jointly with nearby Meppen city), construction of which began in 2007. In August 2011, construction of the ENERCON plant for windpower devices began right here. ENERCON is the manufacturer of the most advanced wind rotors (the actual propellers), producing blades scheduled to deliver 3 MW per unit at the Emsland Euroharbour site. The principal administrative person (*Landrat*) of the largest of the involved counties and cities of Ems Axis, Emsland itself, calls this a “pro-climate climate”, stressing that already now an impressive 82% of the energy consumed in the county are derived from renewables. The location of Euroharbour, the town of Haren (population 24 000), even boasts a 100% renewable electric current production. Among the renewables, wind is most important for Ems Axis region. With the shore nearby and little terrain roughness it is most suited to create onshore wind plants, making northwestern Germany outcompete the southern parts of the country in this respect.

Yet there are also offshore windpower parks in the region now. In 2010, the first one in German domestic waters, “Alpha Ventus”, was erected and connected to

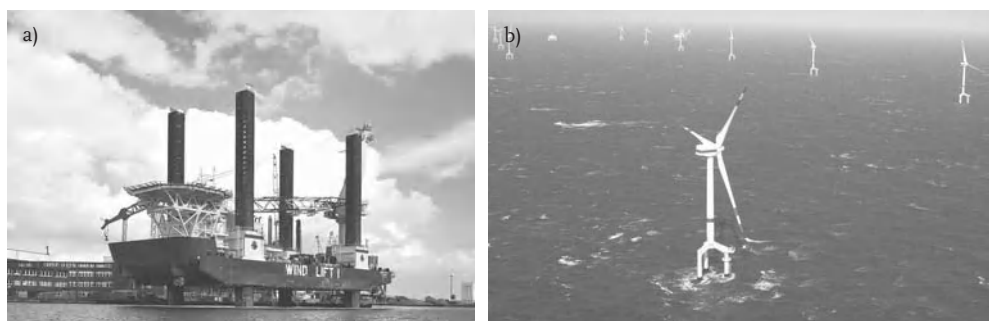


Figure 4.51 BARD Emden Energy GmbH produces rotor parts and so on for offshore windpower plants, then mounting them at sea also. Located at Emden, it belongs to economic region Ems-Axis. (a) German

special crane ship for the setup of offshore wind farms, called *Wind Lift 1* (BARD), in the harbor of Emden (wikipedia, photographer Carschten). (b) BARD offshore 1 (May 2011). Photo courtesy of BARD Group.

the grid. As for crucial parts of wind power technology, BARD Energy at Emden produces both rotor blades specifically designed for offshore application (there are special criteria to withstand salt corrosion, impact of water drops on the fast-moving blades, etc.) and likewise constructs entire powerplants at offshore sites (Figure 4.51).

Suffice this to show some features of the booming Ems Axis economic region, which additionally sports, for example, the Transrapid (maglev) testbed at Lathen and notably a big plant at Werlte going to be the first in the world to convert excess windpower energy via hydrogen and hydrogenation of CO_2 into methane for energy storage purposes (to be combined with natural gas CH_4 and biogas). The Ems Axis consortium stated on issues of energy use efficiency and extending the amount of renewable energy supply in May, 2011:

“Partners in the growing region Ems Axis consider big chances for the local and regional economy to be obtained from making their energy supply a cornerstone of economical politics. Simultaneously they respond to their environmental responsibility by making energy use more efficient and increasing the share of renewable energy sources.

The growing region Ems Axis is capable of becoming a model (blueprint) energy supply region for the future. Concerning Germany, this region both has the largest concentration of windpower plants and is the site of globally active producers of windpower devices. In addition, renewable energy is earned here from all biomass, sun and geothermal resources. So there is a bandwidth of competence in energy supply which yields new impetus to the region by enhanced cooperation and thus advantages in competition which in turn once more improves the economic performance of the local enterprises.”

More pieces of information on the Ems Axis region, including the pertinent enterprises, can be obtained via their homepage www.emsachse.de.

4.4.3

Conclusion

The present mix of renewable resources used in both thermal and electrical energy delivery represents a superposition of both technical problems still to be overcome (the less so) and political decisions, many of which are made in favor of protecting the respective domestic industries for both producing energies and the very power plants required to obtain and convert them: this partly is a quite reasonable and to some extent even responsible industrial policy. Now there are “old” energy sources exploitation of which has become so costly that it is worthwhile only in certain most simple conditions, including hard coal, and in another way, oil sands. This statement refers to all economic costs of exploitation, ecological by-effects (and cultural ones such as destruction of villages and first-nation settlements in favor of open pits) and risks production causes to the workers. The renewables make it to the market step by step with their increasing ability to compete economically and the perspective to relieve old dependences, in addition to avoiding the above risks by offering genuine technical alternatives.

Of course, this might produce problems for countries which have *virtually* nothing else to offer to today’s global markets than their fossil energy carriers including uranium while some of the “bigger shots” in fossil fuels mining are, actually, highly industrialized countries, like the United States, Canada, Australia and Russia. Apparently, however, there is no convincing perspective of sustainable development by which the common populations might benefit from exploitation of fossil energy carriers *alone* for countries like Niger⁹⁸) in western Africa (uranium), or Yemen in the Middle East (oil). Several of the Arab oil-producers are very aware of what might happen to them, their regimes, their population and their common welfare (which is often really restricted to some indigenous minorities) when oil continues to get scarce, and there are warning examples in economic history of countries, societies and national economies running out of the single, principal minable resource on which the entire economy was based, like the tiny South Pacific republic of Nauru (phosphate) and Bolivia in central South America (tin, silver).

Nevertheless, the exchange of our joint economic basis for energy production appears feasible globally within some 50 years from now. It remains to be seen whether this is fast enough both to control climate effects from fossil combustion within acceptable limits, and to reorganize completely our strategies of personal transportation while avoiding yet more catastrophes like those in Chernobyl or Fukushima [but also the failure of a hydropower plant in Longarone (Friaul, northeast Italy) which took some 2000 lives in 1963]. Besides this, nuclear power

98) Other large uranium suppliers like Gabon (West Central Africa) or Kazakhstan (Central Asia/Eastern Europe) have a more diversified supply portfolio.

plants—like other technical systems—can run into operation states where they almost or entirely escape control. If a catastrophic accident then can be avoided due to self-regulation or simply good luck, it is by no means satisfying or consoling that, for example, nuclear reactors got into states which were not even known to their own operators for extended periods of time (like in Forsmark, Sweden, in 2006), let alone these people would be able to influence it anymore.

The future is ahead but notoriously hard to predict; but we are to take chances, severe chances if we decide either way, and we should be aware that doing nothing is tantamount to taking not only chances but pursuing ways we know for sure not to be sustainable, not even in the shorter term.

Glossary

Absorption: Uptake of some gas or liquid into the interior binding places of some porous solid (sponge, pumice, active carbon, aerogels, zeoliths).

Adiabatical: Change of state without exchanging heat energy with the environment. For example, rapid compression of some gas sample—especially in an isolated chamber—causes it to warm up, with the size of the effect depending on the number of atoms in the gas molecules; conversely expansion without external heating means cool down. This also happens in the atmosphere: but slightly moist air ascending into higher (lower pressure) regions will cool down so much as to make the water vapor turn into clouds, even causing thunderstorms.

Adsorption: Fixation of gaseous or liquid or ionic sorbates along (on) some solid (or liquid) surface. Physisorption means just polarization while chemisorption entails some covalent interaction between sorbate and sorbent, often up to an extent where the first (downmost) sorbate layer molecules are completely dissociated and possibly undergo rearrangement.

Advanced oxidation procedures (AOP): This term collects all the methods used to oxidize organic pollutants in aqueous media, employing hydrogen peroxide, ozone, and nonclassical sources of energy, like very short UV radiation (EUV, VUV), ultrasound (sonochemistry) or illuminated semiconductors (photoelectrochemistry, commonly TiO_2) and various catalysts like iron salts.

Ancient cultural concept of *locus amoenus*: *Locus amoenus* (Latin) means pleasant site, a site one wants to dwell at. It comes to no surprise that modern vacation catalogs very often reproduce analogs of this: typically a seashore, but always suggesting an intact mode of interactions among environmental compartments, vegetation and man. (Effluent) ancient Romans tried to create this kind of surroundings in their villas (land inns) and gardens, with fish ponds and so on.

Aquifer: Soil layers percolated by water.

Aromatic compounds: Their reaction kinetics are described by the $\rightarrow$ Hammett equation which was derived about 1935 to describe such reactions during which aromatics exchange electrons with reaction partners (as a rule, give away electrons or electron pairs to the latter).

Autocatalytic: A class of chemical reactions which are promoted by some catalyst—most often H^+ —and release this very catalyst as a by-product of the reaction. For example, acids are produced during oxidations, and many oxidations in turn are prone to acid catalysis. As a result, the reaction rates in some closed vessel (without absorbing the protons by some buffer) will ever increase until the entire substrate has been consumed, then stopping suddenly (clock reactions, e.g., oxidations of HSO_3^- by iodate or chlorate). In more viscous media, often reaction fronts arise. Autocatalysis is a necessary feature for nonlinear chemical dynamics, including oscillations. The classical theory used to distinguish autocatalytic processes from the “chemical background” untouched by this phenomenon, stoichiometric network analysis (SNA), was applied to reproduction and bioinorganic chemistry also, reproduction of cells and entire organisms being a kind of autocatalysis also as enzymes are catalysts and biology (metabolism) in general is a bunch of chemical phenomena.

Belousov/Zhabotinsky system: The eponymous chemical oscillator, first described in 1959. A variety of CH acidic organic compounds (e.g., citric, malonic, cyanoacetic acids, acetylacetone) are oxidized by bromate ion in dilute sulfuric acid solution, the redox process which eventually produces bromohydrocarbons and their respective polycarboxylic acids (e.g., bromofumarate ion) is catalyzed by 1e transfer metal complexes/ions like Mn(III), Ce(IV), or $[Ru(bipy)_3]^{2+}$. The mixture periodically changes from clear to a yellow-orange color, due to periodic enrichment of intermediates bromine and BrO_2 . Oscillations are due to autocatalysis.

Bioaccumulation: Uptake and possible enrichment of chemical elements or certain organic compounds with respect to either source of chemicals: soil (plants, fungi, lichens, soilborne organisms, water (e.g., fishes) or food (animals). Accordingly, there are two different kinds, pathways and terms for bioaccumulation, namely biomagnification (enrichment via food) and bioconcentration (just involving environmental compartments). Unless for unpolar organics and some organometal compounds, “genuine” bioaccumulation is rare; rather, there is a steady decrease of element levels along some trophic chain. Probably this – by leaching via the Gill/water interface – sets a limit to the length of aquatic (limnetic or marine) food chains.

Bioavailability: Many chemical elements exist in the environment, including soil and water, in quite a number of different chemical speciation forms. These may be distinguished by rather different chemical potentials of the respective elements, different ion charges or molecule polarities. Some elements may only be used if they come with certain ligands; for example, most animals cannot use molybde-

num for oxidoreductase unless it comes complete with one pterin ligand. Iodine presenting as iodide or iodate ion is introduced into thyroxine while most organoiodine compounds cannot be converted and even are highly toxic and mutagenic for their alkylating properties. Some complexes of metal ions cannot be resorbed by plant roots or gut membranes while others do quite readily (up to 100%). Elements might not be extracted from certain insoluble salts (phosphates, sulfides) unless for prior microbial attack. So bioavailability, often measured by percentage of oral resorption, can be quite variable. In addition, there are a sizable number of resorption antagonism between pairs of elements, like between Cu and Mo. Toxicity and toxic effects can likewise depend on mode/pathway of uptake: inhaling methanol vapor will not do you much harm, while drinking a few milliliters will cause blindness; and with liquid mercury metal it is rather the other way round.

Bioconcentration factor (BCF): The relative factor by which a compound or ion becomes enriched upon passing from soil, ambient water (aquatic organisms), or food into the test organism. Usually BCF depends on the site or organ of test organism which is sampled (organotropy). The BCF is limited by all resorption kinetics, physicochemical properties of the chemical species to be resorbed and its possibly being abandoned by excretion, volatilization or metabolic transformations. In higher organisms, few resorbed chemicals are to stay there “forever”.

Biofortification: Attempts to increase the nutrition value of food or fodder by treating/growing it in a way as to increase the contents of certain essential minerals or vitamins (“golden rice”) or amino acids (e.g., lysine in corn). Ways to achieve this include all growing in high-metal soils, additions to the soil and genetic engineering.

Bioindicator: Organisms or communities of organisms whose content of certain elements or compounds and/or whose morphological, histological or cellular structure, metabolic-biochemical processes, behavior or population structure(s), including changes in these parameters, supply information on the *quality* of the environment or the nature of environment changes.

Biomineralization: Production of minerals by living matter. Respective products include CaCO_3 (both aragonite [molluscs] and calcite), Ca phosphates, silica, SrSO_4 (some foraminifers), dolomite, magnetite Fe_3O_4 (for processing magnetic signals) and some others. Products of biomineralization include structures such as clam and snail shells, teeth, vertebrate skeletons, the (collective) shielding of coral polyps.

Biomonitor: Biological test system used to determine effects of chemicals imposed on some organism in *quantitative* terms. This can be done by either measuring the amounts which pile up in the organism directly or those of certain metabolites or enzymes induced by the presence of the said compound or metal ion.

Conversely inhibition of some enzyme by action of a toxic antagonist might cause metabolic intermediates to enrich (e.g., δ -aminolevulinic acid if Pb^{2+} blocks porphyrine ring biosynthesis from it) which also can be related to exposition in quantitative terms. Anyway, the essence of biomonitoring is quantitative determination of environmental chemicals through organisms, be it by direct chemical analysis or derived, effect-related methods (*effect biomonitoring*).

BOD: Biological oxygen demand. BOD means that amount of dioxygen required to oxidize all the compounds dissolved in 1 l of test water for complete biological oxidation, that is, as far as biological oxidation will proceed (here, chloroorganics produce Cl^- at best, but not chlorine or even ClO_4^- as these states of Cl cannot be reached by biological oxidation). Substances which do not undergo biological oxidation do contribute to the measured BOD value (thus, the difference between $\rightarrow$ COD and BOD). If BOD is far in excess of dioxygen solubility in water (some 10 mg/l), the water is strongly polluted and can no longer be purified by organisms unless additional oxygen is administered by pouring air through the water or by photosynthesis.

Carbon capture and storage (CCS): Normally, CO_2 produced during combustion of some fuel is vented into the air directly. This should be avoided given: (i) the greenhouse effect due to this gas and (ii) its potential to decrease the pH value of ocean waters, even to the point that the stability of CaCO_3 biostructures (clam shells, corals) becomes difficult. Hence it is tried to withhold CO_2 from the atmosphere, including its removal from combustion production gas flows ("capture") and then relocation into some permanent withholding site far from the atmosphere ("storage"). Several methods are being investigated and tried especially for the latter purpose.

Cengis (other transliteration: Genghis) Khan: (Originally Temüjin). Mongolian ruler (about 1162–1227) who united the competing tribal areas to form a kingdom controlled by himself and rapidly expanding. The original name is derived from either descendancy of a family working as blacksmiths or coming from Lake Baikal area (*Tenggis* in Mongolian, the present border with Russia being very close to the southeast shore of Baikal). Mongolians now consider him the founder of their state, hence quite different items and institutions now bear his name. Succeeded by his third son Ogedei. The large number of casualties also among civilians in his military campaigns became notorious.

Chemical equilibrium: Final state of a (reversible!) chemical reaction when "forward" and "backward" product undergo identical turnovers per unit of time and volume. Although now apparently nothing happens anymore, reactions keep going on as evidenced, for example, by isotopic exchange experiments (labeling either some educt or product by uncommon or radioactive isotopes causes the isotopic label and possible radioactivity to be found distributed over all the chemical species involved in this equilibrium sooner or later).

Chemocline: In both water and soil, there may be rather abrupt changes of redox potential and chemical composition of water bodies ([ground-] water). For example, the salt content of water may rise downward, precluding mixing of vertically overlying layers by convection, or/and dioxygen, nitrate may be depleted, causing organisms to consume sulfate and produce H_2S , such as in the Black Sea. The usually thin transition layer is the chemocline. Chemoclines may be temporary, due to inhibition of mixing by temperature gradients, or permanent. Upon ripening of soils in the decades after deposition, chemoclines are also produced in a manner of self-organization.

Chemolithoautotrophs: Organisms—almost exclusively¹⁾ unicellular ones—which use “minerals” for running central metabolic redox reactions (rather than taking O_2 as an oxidant). Presumably, several of these metabolic pathways predated the advent of dioxygen in Earth’s atmosphere some 2.3 bio. years ago. The respective “minerals” employed as terminal electron acceptors (TEAs) include metal oxides (Fe, Mn, U) as well as oxoanions of nonmetals (nitrate, arsenate, sulfate). These TEAs are used to oxidize H_2 , H_2S , Fe^{2+} , CO, various organics—depending on the TEA—and gain metabolic energy from it. Chemolithoautotrophs are autotrophic organisms, producing their organic matter from CO_2 (or CO) even though they might obtain the electrons to do so from yet other organic compounds. CO_2 fixation is accomplished by Rubisco enzyme, quite like with photosynthetic organisms. Anoxygenic photoautotrophs (i.e., photosynthetic bacteria which likewise oxidize Fe(II) or H_2S [thiorhodacees] but do so in a photochemical manner) are normally not counted among the chemolithoautotrophs. There can be aerobic chemolithoautotrophs, such as diverse iron bacteria.

COD: Chemical oxygen demand. The theoretical amount of oxygen which would be required to oxidize completely the organics and some other compounds dissolved in 1 l of test water. The COD is an equivalent value determined from consumption of dichromate under standard conditions. COD refers to some 95–97% of all organics which can be oxidized in aqueous medium. Other imaginable oxidants are either more selective (peroxodisulfate, periodate IO_4^-) or somewhat more comprehensive (alkalinic permanganate, ferrate FeO_4^{2-}) albeit on the expense of poor titration reagent stability and/or uncontrolled and irreproducible co-oxidation of inorganic constituents.

Co-metabolism: Some persistent substrates of metabolism will not be processed as such, alone, but only—if not always readily—if another substrate, often glucose or ethanol is added. Metabolic degradation thus happens in a coupled mode only,

1) Quite recently, a group of metazoan animals was discovered which can maintain life over entire generation cycles by reducing sulfate rather than consuming oxygen (*Loricifera* in a hypersaline, anoxic sea bottom depression near Crete; Danovaro

et al., 2010). With respect to their elemental composition, these creatures show stunning peculiarities even when compared to their close relatives in aerobic surroundings. Most remarkably, they can apparently *do without magnesium*.

sometimes due to secondary metabolism. This can be due to secondary metabolism, that is, coupling of unpolar $\rightarrow$ xenobiotics to polar substrates (glycine, sulfate) or oxidation products thereof (glucuronic acid, made *in vivo* from glucose).

Donor atom I and II: Ligands form chemical bonds towards metal ions or -atoms, and these chemical bonds are associated with certain linking atoms, much like with covalent organic or inorganic compounds. In metal complexes, these linking atoms in larger, polyatomic ligands (say, amino acids) are called donor atoms. In amino acids including EDTA, there are two different kinds of donor atoms, namely, nitrogen (in the amino groups) and oxygen (carboxylate). These different atoms can of course be distinguished and (albeit a little arbitrarily) numbered, for example, according to relative complex binding stabilities.

Ecotone: Borderline and connection between two ecosystems. Sometimes it can be seen obviously in the landscape, like with lake shores or the edge of some forest, while in other cases (especially when located underground or submerged in water) it is more to chemical differences which may or may not permit certain organisms to live there, producing a “discontinuity” in biocoenoses. Examples of this kind include the oxycline (if existing permanently in some body of water, like the Black Sea), or differences in soil chemistry: the edge of a serpentinite region is chemical in origin (very high heavy metal, Al and Mg contents, “strange” soil pH) but likewise produces a visible signature in vegetation cover (adapted ferns, scrubs, no woody plants).

Electric work function (EWF): The minimum quantum energy required to “kick out” photoelectrons from an interface of either metals or semiconductors (external photoeffect). Its value ranges from about 2 eV ($\lambda_{\max} = 620 \text{ nm}$) with alkali metals or their suboxides like Rb_2O up to some 6 eV ($\lambda_{\max} \approx 210 \text{ nm}$) in platinum or rhenium. P-type semiconductors have even higher values. The EWF is also pertinent to intermetal or intersemiconductor contacts, for example, in Seebeck-type thermoelectric devices.

Electronegativity (EN): EN is the capability of some atom or functional group ($-\text{CF}_3$, $-\text{O}-\text{TeF}_5$) to attract negative partial charges in a larger network of atoms; it thus controls charge distribution within some molecule or molecular ion, including coordination complexes. It is given by empirical scales from Pauling or Allred and Rochow. EN then ranges from some 0.9 (Rb, Cs) to some 3 (N, reactive noble gases Xe, Kr), 3.5 (O) and 4 (F). Of course, the concept of EN does not only hold in the ground (unexcited) state of some molecule but also for charge distribution in excited states. An extreme case is $\rightarrow\text{LMCT}$ excitation of a complex: as the latter includes complete transfer of an electron from the ligand to the metal center, the amount of energy required to accomplish this kind of (photochemical) charge transfer itself becomes a measure of EN of both binding partners. This property accordingly is called optical EN. EN values of anionic ligands are next to those of ground state atoms ($\text{F}^- = 4.0$, $\text{Cl}^- = 3.0$, $\text{Br}^- = 2.75$, $\text{OPh}^- = 3.4$, $\underline{\text{SCN}}^- = 2.6$, $\underline{\text{NO}_2}^-$

and other N donor ligands about 2.9) while those of metal ions in thermally stable complexes are considerably lower (mostly <2.3).

Essentiality: Some organism (taxonomic species) requires administration of a certain chemical (element, “vitamin”, essential amino acid, cofactor) for sustaining life or even reproduction as it cannot produce it itself. For metazoans, some 20–25 chemical elements are essential, including nonmetals C, N, O, H, S and P, and almost always metals K (which sometimes can be fully replaced by Rb), Mg, Ca, Mo (or W instead), Mn, Fe, Cu and Zn.

Eutrophication: (literally: excessive fertilization). Eutrophication refers to an increased input of nutrients for plants (usually phosphate and/or nitrate, but likewise metals such as Fe [in the oceans] or Mg [in “soft” freshwaters]) into some body of water, causing plants—especially plankton algae—to display enhanced growth. A while afterwards, the plant materials which die off can no longer be oxidized using the amount of dioxygen which can be dissolved in water ($\leq 300 \mu\text{M}$ [$l; \rightarrow \text{BOD}$]), but rather they sink to the ground, causing sulfate to be reduced after the O_2 is used up completely. Sulfate reduction affords H_2S which is highly toxic to vertebrates, as is NO_2^- , the first product of parallel or preceding nitrate reduction. Only a few species of fishes, like *Carassius carassius* (capable of ethanol-making fermentation) or pike-perch *Schizostedion lucioperca* can “dive” into such water regions (where they cannot breathe by their gills, quite like we cannot breathe when [apnea]-diving underwater) while the others become asphyxiated. Large-scale fish kills are typical of this situation, called the “ecological collapse” of a water body. This may also happen in large-scale, nonmeromictic water bodies like (bights, fjords of) the Baltic Sea.

Fenton reaction: An oxidation reaction first described in 1894 which is caused by combining oxidant hydrogen peroxide H_2O_2 —which would not bring about most of these reactions alone—with *reductant* Fe^{2+} . Contrary to earlier beliefs, the reactive species is ferryl(IV) $[\text{FeO}]^{2+}$ rather than a OH radical. The Fenton reaction can be used for almost complete degradations of many different organics including pollutants exactly due to this [ferryl(IV) will open aromatic rings, unlike OH].

Fischer-Tropsch type chemistry: Hydrogenation of CO or CO_2 by compressed H_2 to produce hydrocarbons (CH_4 through gasoline HCs up to long-chain alkanes and alkenes) and alcohols (methanol, ethanol, ethanediol, long-chain alcohols), catalyzed by various solid interfaces (heterogeneous catalysis); the byproduct is water. These interfaces include Fe and Cr oxides, Ni metal, iron meteorites (!), metal ferates and influence both the temperature (commonly, 200–300 °C) and pressure (commonly, 5–100 bar) in which the transformations take place, and the spectrum of products to be formed (e.g., on nickel or Ni/ ZrO_2 almost pure CH_4 , and CH_3OH , respectively, are formed). Some amounts of carboxylic acids and—if amines are added—formamides and amino acids are also formed (Hayatsu, Studier, and Anders, 1972). The Fischer–Tropsch reaction is reversible, then used for producing

hydrogen in processing fossil fuels before using them in fuel cells where H_2 is much easier to use (avoiding PGM electrodes) than any hydrocarbons or alcohols.

Fischer and Tropsch were German chemists in the 1920ies, the scale-up of the process ending in the large Leuna (Saxony-Anhalt) plants for gasoline production from lignite (lignite being preconverted into $CO + H_2$ by treating it with hot [$\approx 1000^\circ C$] water vapor), producing several thousand tonnes/day of liquid hydrocarbons. The plants remained in use through WW2 and GDR times until 1990, only then abandoned. Instead of lignite, biomass, sewage sludge, or garbage can be treated the same way to obtain fuels.

Grotthus–Draper’s law: Even before the law of conservation of energy was ever formulated, early photochemists noted that there were only transformations of chemicals by light or UV energy if it was in spectral bands actually absorbed by the substrate. Both liquid ammonia and water are exothermic compounds, yet pure water is rather stable towards photolysis as there is no absorption above $\lambda \approx 200\text{ nm}$, while NH_3 does absorb in a broad region of longer UV, causing rapid photolysis (also in gas phase). In photochemistry including chemical (nondigital) photography, photochemical reactions can be introduced by addition of sensitizers (some kind of dye) which absorb in other spectral bands than the primary substrate and then exchange energy or electrons with the latter.

Hammett equation: $\log k_i - \log k_0 = \rho_j \sigma_i$, with σ_i being a substituent constant, $\log k_0$ the reaction rate measured for the prototype compound benzene ($R = H$; $\sigma_i = 0$) in the given conditions, and ρ_j denoting a reaction constant. The Hammett equation gives a relationship between reaction rates of substituted aromatic (benzenoid [benzenes, fluorenes, biphenyls] or naphthenoid [naphthalenes, acenaphthenes]) hydrocarbons towards a specific electrophilic (say, CH_3-CO^+ , $HCNH^+$) or radical (OH , NO_3) reagent, for example, a nitration by $(NO_2)BF_4$ in acetonitrile solution run at $60^\circ C$. This (logarithmic) reaction rate is then compared to that of benzene (or the other parent aromatic hydrocarbons, respectively) making use of the mentioned substituent constant R which denotes the effect caused by the substituent R located in either meta- or (more commonly) para-positions. The R (e.g., $-CH_3$, $-CN$, $-C(O)OCH_3$, $-OH$, F , NO_2 or CF_3) display fairly constant effects for 3- and 4-position substitutions, respectively, producing the above equation $\log k_i - \log k_0 = \rho_j \sigma_i$. The reaction constant depends on all kind of reaction (acetylation, nitration, radical hydroxylation, etc.), kind of solvent and temperature (the latter two contributing to the activation barrier, for our example purpose: nitration in acetonitrile at $60^\circ C$). According to the fact that only some small fraction of encounters will cause reaction, and the sign of activation energy, ρ_j is usually negative, whereas σ_i can be between about -1.4 and $+0.9$. The equation is named in memory of its creator, Louis Plack HAMMETT (1894–1987).

Heavy metals: Metallogenic elements having elemental densities $>6\text{ g/cm}^3$. For more than a century now (first paper in 1904), certain toxic properties were associated with heavy metals, but this is but partially correct: besides rather harmless

heavy metals, like most rare earth elements (except of Nd, Tb and Eu which latter is not a heavy metal at all) there are highly toxic non- (As, Sb) and light metals, particularly Be. While there are limiting values of 5.0 and even 4.5 g/cm³ in the literature, the upper limit of 6.0 g/cm³ is selected for quite a number of chemical arguments. All transition metals and REEs excepting scandium (Sc), yttrium (Y), titanium and europium are heavy metals, as are all the actinoids (Ac to Lw), while among main-group elements having ambient-pressure metal allotropes²⁾ these are but tin (Sn), lead (Pb), indium, thallium and bismuth while Sb, and At are not actually metals. There is (Fränzle and Fränzle, 2002) a chemical relationship between the “toxicological nondescript” term (Nieboer and Richardson, 1980) “heavy metal” and reduction into a metal being fairly easy (that is, behaving as a noble metal): electron shells of heavy atoms do contract because the strong attraction by nuclear charges $Z \gg 50$ is increased by relativistic effects (binding energies of innermost electrons of 10–20% of their rest mass make the orbitals shrink further).

Ianus face: Ambiguity: the same phenomenon has two different features, a “nice” one and a problematic one. For example, isotopic fractionation techniques coupled to nuclear fission can be used either to obtain energy and to produce devastating (nuclear) bombs, while organophosphorus chemistry can be employed either to make alkenes and cytostatics, including pharmaceuticals, or to produce chemical warfare agents (“nerve gases”).

IGCC: A process derived from steam reforming, making a mixture of H₂ and CO or CO₂ from other fossil or biogenic fuels. The hydrogen then is used in fuel cells or internal combustion engines/gas power plants, while CO₂ is captured and deposited (→ CCS).

Iron Curtain: Both a metaphor (obstacle for the free travel of people, items and ideas, information) and denoting the actual borderline fortifications meant to keep people from fleeing from the then Communist Eastern Europe to the West (rather than protecting against hypothetical Western [NATO] military attacks). The term was coined by Churchill in late 1945 and later transferred and adapted (e.g., “Bamboo curtain” referring to politics in Communist south eastern Asia).

Isomer: When atoms form more than two bonds towards other atoms, they can arrange in networks (different molecules) which contain different topological arrangements of the heavier atoms (other than H, halogens). Isomers can be both closely related (say, *n*-heptane, 3-ethylpentane, 2,3-dimethylpentane, etc.) or rather unlike [say, the C₂H₅NO₂ isomers glycine NH₂–CH₂–COOH, nitroethane and

- 2) Many nonmetals turn into metals upon thorough compression at $P > 200$ kbar, for example, oxygen, iodine, arsenic and even xenon, besides lots of semiconductive binary compounds (while some metals behave conversely, becoming

semiconductors in high pressure, like ytterbium). Even though the corresponding densities are about 6–8 g/cm³, these elements and compounds are not considered heavy metals.

acetoxyhydroxamic acid $\text{CH}_3\text{--C(=O)--NH(OH)}$. Isomers can also be formed by anions (the classical cyanate/fulminate $[\text{NCO}^-/\text{CNO}^-]$ couple identified by Liebig) or complexes, with ligands arranged around some metal center in unlike ways, such as *cis*- and *trans*- $[\text{RuCl}_2\text{Br}_4]^{2-}$. Of course, isomers used to differ in both chemical potential (internal energy) and stability, up to the point that one or more will no longer persist and thus can be isolated only in special conditions or may rearrange or decompose violently. However, isomers must be isolable “in principle” from some mixture rather than being mere transition states.

Kirchhoff's theorem: If there is a branch inside some flow system, for example, a bi- or multifurcation in some part of an electric circuit, or the two branches of a river on either side of an insula, flow rates of electrons or water will be reciprocally equal to the respective drag values (electrical resistivity or hydraulic drag); for example, when there are two branches of wire in a circuit, two-thirds of total current will flow through the branch having half the resistivity of the other. Kirchhoff's theorem must be taken into account whenever the resistivity of some subsystem is to decrease considerably during operation to avoid destruction of a device, for example, when igniting a gas discharge or heating a semiconductor filament.

Kondratieff cycles: The periods of time shaped by some specific technology. Typical approximate timeframe: 1770–1830 (coal use, steam engine), 1830–1880 (locomotive), 1880–1930 (telephone and electrical grids, chemical industry), 1930–1975 (transportation [car, airplane], use of light metals and plastics), since 1975 information technology (computers, Internet).

Kondratieff-type long waves: There is evidence for long-term periodicity in global raw material and commodity prices over centuries, the length of period being some 55–60 years. Although this was noted earlier, this discovery (thus the name) is usually credited to Soviet economist Nikolai D. Kondratieff (1892–1938) in 1926. The reasons for this periodicity are a matter of much debate, but each of the Kondratieff long waves and → Kondratieff cycles is associated with a key technological innovation (using coal for making steel, the invention of steam engines and locomotives, the telephone, electricity grids, large-scale use of light metals, cars, airplanes, computers). Apparently the kind of synchronization and feedback seen in Kondratieff waves and cycles is due to globalization which started with large-scale colonial trade in the early eighteenth century. Moreover, feedback can cause selection of one key technology for about half a century, causing the “losers” to lag behind before eventual large-scale application (if happening at all) for about this period of time in a way rather similar to Eigen's structure of hypercycles in chemical evolution (Fränkle and Grossmann, 1998).

Koobi Fora: The oldest known—though somewhat disputed—evidence of a hominid-constructed shelter (a “hut” circumscribed by some thorny branches like a kraal rather than the nests built by apes just to spend the next night in) at a site in Kenia (East Africa) some 2.6 mio. years ago and thus assigned to *Homo habilis*

or *Homo ergaster*. Older australopithecines like *A. afarensis* at River Hadar Valley, Ethiopia ("Lucy") apparently did not build similar shelters against being predated themselves.

Kuiper belt objects: Smaller bodies orbiting in the outer solar system (from the orbit of Neptune [some 30 AE] outwards); maximum diameter about 2500 km (largest ones: dwarf-planets Pluto, Eris, Haumea, and Sedna, captured Neptunian satellite Triton, most of which even have atmospheres). Very small total mass (maybe 2–4 times that of our Moon), but having most of the Solar Systems total rotational momentum; hence Sun rotates very slowly. Except for Triton, Pluto and its largest moon Charon, these very dim objects were only discovered in 1992.

Lambert–Beer law: The rule which links the extent of light absorption (absorption ϵ) to spectral properties of the absorbing species (extinction coefficient E), the concentration of solution (c) and thickness of absorbing layer (d):

$$\epsilon = E \cdot c \cdot d$$

The scale is logarithmic: when 1 m of pure absorbs 50% of red light ($\epsilon \approx 0.7$), then 2 m absorb 75% ($\epsilon \approx 1.4$), a 3 m thick water layer 87.5% ($\epsilon \approx 2.1$) and so on.

LD₅₀: The concentration (water, air) or amount (oral, transdermal, injection application) of some chemical which kills half (50%) of test organisms within a predefined period of time (usually either 48 h or 30 days).

Ligand: Binding partner of a metal ion or –atom, usually donating (at least one pair of) electrons to it. Can be a molecule (NH₃, R-CN, CO) or anion (Cl[–], CN[–], R-COO[–], glyc[–]), rarely a cation (e.g., (CH₃)₃S⁺) or atom (xenon). The stable (depending on solvent and temperature) association of one metal ion and a couple of (commonly, six or four) ligands is called a complex. One ligand can bind to a metal ion via multiple (chelating ligand, glycinate or citrate), or alternative (linkage isomerism, $\underline{\text{NCS}}^-$ or $\underline{\text{SCN}}^-$) atoms or link two or more metal ions (bridging ligands).

LMCT: ligand to metal charge transfer: intense absorptions in transition-metal and f-block (REEs, actinoides) element complexes of mainly higher metal center oxidation states. In a LMCT transition, a metal–ligand bond is photochemically cleaved by transfer of one electron from the (anion or molecule) ligand to the (thereafter reduced) metal center. LMCT states are short-lived ($T \leq 10^{-8}$ s) but intense; they may extend from far UV even into the near IR range (some 1050 nm), however IR LMCT transitions are only detected in complexes which are so "stretched" (combining oxidizing cat- and fairly reducing [ligand-] anions) that they slowly decompose thermally, without any optical excitation. Recombination of charges from LMCT states may be avoided by adding a semiconductor sorbent whereas escaping ligand radicals like OH might react with external solutes like organics.

log k_{ow} : Octanol(1)/water partition coefficient, logarithm of. Denotes polarity of some compound or ion. The most polar neutral organics, like methanol or ethylene glycol, have $\log k_{ow} \approx -2$ (i.e., the equilibrium concentration obtained in the aqueous phase after vigorous shaking is about $10^2 = 100$ times larger than in octanol), while there is no real upper limit (for very unpolar organics like PCBs, $\log k_{ow} = 7$, meaning the octanol concentration level to be ten million times larger than the residues in water). $\log k_{ow}$ is related to all aqueous solubility, bioaccumulation behavior and narcotic (incapacitating) action towards aquatic organisms (first tests on tadpoles dating back to 1899) of organic compounds. For salts (e.g., TEA or TBA salts), the range of possible $\log k_{ow}$ is somewhat shifted.

Lower Mekong area: At some 5000 km total length, River Mekong is shorter only than the rivers Nile and Amazon. The lower Mekong area circumscribes its parts in Cambodia, including the large connected lake Ton Le Sap, and in Southern Vietnam.

Marcus equation: The Marcus equation reveals the relationship among three entities, namely:

- 1) The free energy released by a spontaneous redox reaction, which is tantamount to the electrochemical potential difference of the reaction partners;
- 2) The minimum distance among the involved partners, that is, the atoms among which electrons are exchanged;
- 3) The rate (speed) of reaction.

Because in quantum chemistry electron transfer sensitively depends on distance and the shape of a possible barrier (electron tunneling), only rather similar systems can be compared meaningfully where dimensions and possible bridging groups match. In environmental chemistry, such a study was done (Mártire and Gonzalez, 2000), for example, for the oxidation of phenols including tyrosine by singlet oxygen in aqueous solution. The equation is named after Rudolph A. Marcus (born in 1923; chemistry Nobel laureate in 1992).

Martian atmosphere: Atmosphere of our outer neighbor planet Mars. Much thinner (surface pressure about 6 mbar) and colder (average -55°C) than ours, it mainly (some 95.3%) consists of CO_2 , with the remainder constituted of N_2 , Ar, O_2 , CO mainly (2.7 down to about 0.1%) and quite a number of trace gases including CH_4 , H_2O_2 , and HNO_3 . The origins and sinks of methane (10–30 ppb) are much disputed while other trace gases vary rapidly in their levels (CO, O_2 , water vapor). It is moist and cold enough to support some snow falls as was recently detected.

Moengke Khan: Mongolian ruler and conqueror (1209–1259). Grandson of Cengis (Genghis) Khan.

O^1D : Denotes a certain, highly reactive excited state of the oxygen *atom*. As a rule (Hund's rule) electrons are distributed among orbitals outside of chemical bonds

in a manner as to occupy the utmost number of different orbitals, thus each but singly, and it takes additional energy to combine two electrons (the maximum-number) in one given orbital. The number 1 denotes a singlet state, lacking any unpaired electrons, like in a stable molecule (for comparison, the ground state of atomic oxygen is triplet O^3P having two unpaired electrons). P and D are symbols for principal quantum numbers attributed to the electrons. Spin pairing in O^1D spells taking up the excess energy which can—and usually will—be released when hitting another molecule and react with it: water vapor produces two OH radicals, whereas in liquid water H_2O_2 is selectively produced.

Photoelectrochemistry: (PEC) was discovered as early as 1839 (on a selenium electrode) and rather broadly investigated around about 1925–1935 (about the same time when pioneers of quantum chemistry laid the fundamentals to understand what is going on in an illuminated semiconductor and what is typical of some semiconductor in general) but then was abandoned once again until the 1960s. Now there are applications in purification of both air and aqueous media (embedding media need not be electrolytes as charge separation and transfer occur within the SC particles), besides of organic chemistry. Mostly titania is used for the purification of both water and air. PEC also operates in adsorbed gases and isolating solids as it does not require long-range charge transport outside the semiconductor particles, a fact which probably has also drawbacks in cosmochemistry, but there also is a role for other semiconductors. An exhaustive oxidation, that is, mineralization, of pollutants is only achieved by using valence band holes—and thus semiconductors—which have (aqueous, pH = 7) VB potentials above some 2V versus SCE, thus are capable of transforming benzenoid hydrocarbons into radical cations directly, removing carboxylate or amino groups and so on. Such materials are stable in water against photocorroding themselves only if they are oxides (or fluorides) of valve metals which essentially reproduce and repair their interfaces by hydrolysis of intermediately formed metal cations.

Platinum group metals (PGM): The group of noble metals (only palladium can be dissolved using but nitric acid) which are similar in its properties to platinum (or even were isolated from raw ore platinum [Ir, Os, Ru]). Besides the six stable though very rare elements (abundant in some meteorites but now mostly “buried” in core of Earth), ruthenium, rhodium, palladium ($Z = 44–46$), osmium, iridium, and platinum itself ($Z = 76–78$), the PGM group now includes three more man-made, short-lived highly radioactive elements (hassium, meitnerium, darmstadtium; all made first at GSI, Darmstadt, Germany; $Z = 108–110$). Among these, however, chemical properties were investigated for Hs ($Z = 108$, eka-osmium) only and its chemical features are actually similar to Os and Ru. So it is a PGM indeed, though all of its isotopes which can be directly prepared have half-lives <1 min.

Pleistocene ancestors: Early hominids (human beings) who lived in the Pleistocene (from some 2 mio. years ago, i.e., by end of Pliocene, up to the last Ice

Age), that is, the human species *Homo habilis*, *H. ergaster*, *H. erectus* and others, but not the Australopithecines.

Pourbaix Diagram: A diagram which displays speciation forms of some chemical element E which are thermodynamically in aqueous solution at given pH and redox potential, e.i. when there is nothing but E, O, and H. The P. describes for example, which is the stable form of Mn at pH = 9 and a potential of +0.6 V (MnO_2). There are extended Pourbaix diagrams giving the stable phases when there are additional elements like phosphorus, sulfur, chlorine, or carbon and so on, likewise for non-aqueous systems (thus, omitting O) or different temperatures. All the species depicted there refer to prominent *equilibrium* species, thus, for example, SO_2 , HSO_3^- , or nitrogen oxides will be missed here. Conversely, this shows an excess of free energy that these chemical species, available from smoke gases, will readily be processed into stable products (N_2 and sulfates, respectively), offering chances for (also catalytic, given the processes are obviously exothermic) gas purification. Superposition of Pourbaix diagrams shows which species of different elements will stably co-exist, telling the perspectives of, say, reactive-wall sanitation (Pourbaix diagram of Fe superposed onto that of the elements to be removed) or of biological sulfate reduction (lake water deacidification).

QSAR (quantitative structure–activity relationship): A collection of methods meant to link features of chemical structure (bond network topology, substituents, redox potentials) to some kind of chemical activity. The latter may be some chemical feature like a reaction rate, but also a toxicological one such as killing (toxicity) or narcotic potentials. While “classical” QSAR, be they topological (e.g., the Hückel approach) or functional group-focussed (the $\rightarrow$ Hammett equation), usually dealt with (at best, hetero-)aromatic compounds, modern approaches drawing upon numerical quantum chemistry can also deal with aliphatic and inorganic reactants. QSAR are used to estimate/predict both reactivity and ecological impact of some chemical getting into the environment or produced there.

Rare earth elements (REE): A mis-nomer for lanthanoides ($Z = 58\text{--}71$, Ce to Lu) and trivalent metals (Sc), Y, La itself and Ac. It means metals forming rare oxides (“earths” in old terms), and thus being purported to be rare themselves. Rather, REEs are spread all over the Earth’s crust, commonly in quite similar but not really small concentrations, except for some sites where there are minerals formed by them (monazite, euxenite, gadolinite, etc.), mostly phosphates.

Reactive wall: A ground(water-)located array which can be percolated by water and where some reductant is placed into a water flow to remove and detoxify dissolved pollutants by either reductive precipitation, formation of covalent bonds or insoluble salts. Commonly, the reactive agent is iron scrap, less often so compost or straw. Reactive walls are used against a multitude of groundwater contaminants, from heavy-metal and As salts up to organohalogenes and nitrocompounds.

Ruzicka reaction: A versatile preparative reaction in organic chemistry: two molecules of carboxylic acid are joined to form a symmetrical ketone, CO_2 , and water. From dicarboxylic acids, cycloketones (rather than polymers) arise, including macrocyclic ones (like musk ketone cyclopentadecanone), and this is the most important application for the reaction: $2 \text{ R-COOH} \xrightarrow{\Delta} \text{ R-CO-R} + \text{CO}_2 + \text{H}_2\text{O}$

In technical chemistry, the most common catalyst is modified thoria (ThO_2), while in laboratory-scale preparations alkaline earth carbonates (rather than replacing the neat acids with their salts/anions) or La_2O_3 are used. Leopold Ruzicka (1889–1976) was a Swiss chemistry Nobel laureate coming from Croatia (then Austro-Hungary).

Schottky diodes: Diodes which act as current rectifiers but do not consist of a pn-junction linking two different or two differently doped semiconductors but consist of some (mostly n-type) semiconductor attached to a metal. In fact, rectifiers of this kind were invented back in the nineteenth century and used decades before Schottky and Mott unraveled the principles of operation, then using naturally grown pyrite crystals (FeS_2) as the semiconductor part.

Schrader's formula: One of the first empirical studies on relationships between features of chemical structure and toxicity of a larger group of compounds, namely, halophosphate, pseudohalophosphate (e.g., NC-PO_3^{2-}), and alkyl phosphonate diesters. Schrader, then (1936–1937) with German IG Farben, found that, depending on the structure, both insect and mammal neurotoxicities would differ by several orders of magnitude, but not always in the same trend. Thus, less-toxic (predictably so, using Schrader's formula) species would be used as insecticides, for example, arylphosphonates such as malathion while the most toxic fluorophosphate and methylphosphonate derivatives, for example, sarin and soman, came to be abused as CW agents ("nerve gases"). → QSAR

Speciation: Partition of some chemical element among different modes of chemical bonding or/and oxidation states in an environmental compartment. Besides the thermodynamically stable species shown in a → Pourbaix diagram (then there is partition only when residing on some intersection line or triangle in the Pourbaix diagram), there are additional thermodynamically unstable (S and N oxides) and, mostly biogenic, organoelement forms of binding. Speciation and speciation analysis are often confused, not just in everyday laboratory bench jargon but even in scientific papers: while speciation denotes that chemical or biochemical process turning a chemical into some defined form of binding, speciation analysis is the very analytical procedure employed to identify and quantify binding (speciation) forms which are present, for example, in seawater.

Stoichiometric, ecological: Living beings have a rather constant (within some given organ and species) chemical composition, much like individual molecules. This composition is prone to genetic regulation. Most considerations of ecological

stoichiometry, also claimed to be the “theory of living beings from molecules up to the biosphere” (Sterner and Elser, 2002), focus on the three principal biological nonmetals C, N and P, that is, to C/N and N/P stoichiometric ratios. In newer works, including those by the first author, other biological interelement ratios are also analyzed, mainly such which refer to different though coupled metabolic pathways and the bioelements which catalyze them. For example, since photosynthesis both takes Mg-dependent CO₂ binding and reduction and Mn-dependent water oxidation, the Mg/Mn ratio does not vary wildly in terrestrial plants but is fairly constant, whereas the Ni/Mo ratio, referring to the extent of N binding from the soil by Mo-dependent nitrate reductase and N cycling by arginase, urease (which latter contains much Ni) is linked to the total nitrogen content of plants.

Stoichiometric network analysis (SNA): A method which can be used to identify autocatalytic processes, features, and substructures embedded in a network of chemical reactions. Besides of properly telling apart biochemical transformations (which are autocatalytic by both reproduction and cell budding) and inorganic processes causing the same reaction (say, in Fe²⁺ oxidation by either air, NO₃⁻, or microorganisms), SNA is also suited to identify risks within chemical technology (many explosions are due to autocatalysis).

Sustainability: A way and principle of tackling the economy. The idea is to reduce the irreversible consumption of nonregenerable goods to the utmost minimum by either recycling or switching to regenerable resources or at least try to behave in a manner leaving future generations the same chances of a decent and prosperous way of life as we now enjoy. This refers to both conservation of resources and to problems of local and global environmental states.

Taft equation: Similar to the → Hammett equation for aromatics, the Taft equation introduces a set of substituent parameters to describe and predict kinetics of (here, addition rather than substitution) reactions to alkenes (olefins). Less comprehensive and with larger error bars than the Hammett approach.

Toxicity: The capability of some chemical or other (e.g., ionizing radiation) agent to kill or incapacitate a living being or keep it from reproduction (reproduction toxicity).

Toxin: Venom. A toxin can either block or deregulate (excess activation, like with auxines) single biochemical functions, transformations or enzymes, act on the entire body or influence reproduction. There are different biochemical modes of toxin action, such as a reaction with the functional center of an enzyme (replacing the meant substrate by reacting to the active center, replacing or introducing a metal ion) or attack some receptor (this is common in endocrinic activity but also neurotoxicity with or without prior stimulating, mood-enhancing or hallucinogenic effects) or to nerve membranes, synapses or signal transduction (Tl⁺, Na channel toxins like tetrodotoxine, saxitoxine and other carbamidines).

Ugedei Khan: Mongolian ruler, son of → Cengis Khan, died in 1241. Mastermind of the expansion of the Mongolian Empire outward (to the west and south west, defeat of New Delhi) of north eastern Asia, but stayed at capital Karakorum (not to be confused with Karakorum mountain range, Pakistan!) for giving central directives after the 1232 battle of Kaifeng, probably for reasons of faltering health. This is why, after his sudden death became known in Central Europe in 1241, Mongolians, who had just won the battle of Legnica (Lower Silesia, now Poland), suddenly abandoned their swift military progress through Ukraine and Poland towards the Atlantic Ocean and returned all the way to Mongolia to see who now was to take charge and whether expansionist politics would be continued (→ Moengke Khan).

Wackenroder's liquor: A yellow to reddish, clear to somewhat turbid solution prepared by passing gaseous SO_2 into a H_2S solution. Besides of thiosulfate, it mainly contains polythionates (sulfur chain disulfonates) of S_3^- up to about S_{20} chain lengths.

White-clover test: Leaves and flowers of white clover are most sensitive towards photooxidants, especially tropospheric ozone contained in → Los Angeles smog. The number of damaged or miscolored leaves gives a hint of ozone burdens.

Woodward–Hoffmann rules: The Woodward–Hoffmann rules, named after chemistry Nobel laureates R.B. Woodward (1919–1985) and Roald Hoffmann (born in 1937), refer to the stereochemistry of ring-forming thermo- and photochemical addition reactions in organic chemistry. Besides, chemical kinetics depend on energy differences among the orbitals involved in one chemical reaction, whether the net result is charge transfer (→ Marcus theory) or formation of covalent bonds (Fukui–Hoffmann rules). As a result, having a complicated molecule bearing quite different functional groups (which in turn are distinguished by likewise different orbital energies and, hence, redox potentials) react with a given reaction partner, there will be selective attack on one of these functional groups. Much of metalloenzyme selectivity also works due to this.

Xenobiotics: Literally: substances alien (Greek *xenos* = alien) to life. Substances which get into the environment and interact with the biota but do not occur naturally. Xenobiotics can become toxic upon this interaction with organisms or persist through it, but need not do so:

- Many enzymes and metabolic pathways can degrade corresponding chemicals in a rather nonselective mode.
- Radionuclides and other substances degrade (e.g., by hydrolysis) as time passes, regardless of their xenobiotic features and modes of action.

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Symbol	Element	Atomic #	Symbol	Element	Atomic #
Ac	Actinium	89	Ir	Iridium	77
Al	Aluminum	13	Fe	Iron	26
Am	Americium	95	Kr	Krypton	36
Sb	Antimony	51	La	Lanthanum	57
Ar	Argon	18	Lr	Lawrencium	103
As	Arsenic	33	Pb	Lead	82
At	Astatine	85	Li	Lithium	3
Ba	Barium	56	Lu	Lutetium	71
Bk	Berkelium	97	Mg	Magnesium	12
Be	Beryllium	4	Mn	Manganese	25
Bi	Bismuth	83	Mt	Meitnerium	109
Bh	Bohrium	107	Md	Mendelevium	101
B	Boron	5	Hg	Mercury	80
Br	Bromine	35	Mo	Molybdenum	42
Cd	Cadmium	48	Nd	Neodymium	60
Ca	Calcium	20	Ne	Neon	10
Cf	Californium	98	Np	Neptunium	93
C	Carbon	6	Ni	Nickel	28
Ce	Cerium	58	Nb	Niobium	41
Cs	Cesium	55	N	Nitrogen	7
Cl	Chlorine	17	No	Nobelium	102
Cr	Chromium	24	Os	Osmium	76
Co	Cobalt	27	O	Oxygen	8
Cp	Copernicium	112	Pd	Palladium	46
Cu	Copper	29	P	Phosphorus	15
Cm	Curium	96	Pt	Platinum	78
Ds	Darmstadtium	110	Pu	Plutonium	94
Db	Dubnium	105	Po	Polonium	84
Dy	Dysprosium	66	K	Potassium	19
Es	Einsteinium	99	Pr	Praseodymium	59
Er	Erbium	68	Pm	Promethium	61
Eu	Europium	63	Pa	Protactinium	91
Fm	Fermium	100	Ra	Radium	88
F	Flourine	9	Rn	Radon	86
Fr	Francium	87	Re	Rhenium	75
Gd	Gadolinium	64	Rh	Rhodium	45
Ga	Gallium	31	Rg	Röntgenium	111
Ge	Germanium	32	Rb	Rubidium	37
Au	Gold	79	Ru	Ruthenium	44
Hf	Hafnium	72	Rf	Rutherfordium	104
Hs	Hassium	108	Sm	Samarium	62
He	Helium	2	Sc	Scandium	21
Ho	Holmium	67	Sg	Seaborgium	106
H	Hydrogen	1	Se	Selenium	34
In	Indium	49	Si	Silicon	14
I	Iodine	53	Ag	Silver	47

Symbol	Element	Atomic #	Symbol	Element	Atomic #
Na	Sodium	11	Sn	Tin	50
Sr	Strontium	38	Ti	Titanium	22
S	Sulfur	16	W	Tungsten	74
Ta	Tantalum	73	U	Uranium	92
Tc	Technetium	43	V	Vanadium	23
Te	Tellurium	52	Xi	Xenon	54
Tb	Terbium	65	Yb	Ytterbium	70
Tl	Thallium	81	Y	Yttrium	39
Th	Thorium	90	Zn	Zinc	30
Tm	Thulium	69	Zr	Zirconium	40

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